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Review

Environmental aspects of fluorinated materials. Part 2*. 'In-kind' replacements for Halon fire extinguishants; some recent candidates

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Abstract

Environmental and in-use characteristics of three potential replacements for brominated fire extinguishants (Halons) are discussed, namely NAF SIII™, FE-13™ and FM-200™. Background information relating to the Montreal Protocol on Substances that Deplete the Ozone Layer, the assessment of environmental acceptability of CFC and Halon replacements, tropospheric decomposition mechanisms and fluorocarbon nomenclature is included.

Introduction†

During the past 20 years it has become widely accepted in academic, industrial and political circles that the release of volatile man-made halocarbons (halogenated hydrocarbons, notably CFCs and Halons††) into the Earth's atmosphere causes depletion of stratospheric ozone [2]. In response to society's concern over potential effects of ozone depletion, a variety of national and international regulations have been promulgated, the best known being the Montreal Protocol on Substances that Deplete the Ozone Layer. This landmark international agreement, introduced in 1987, has already been revised twice (London 1990; Copenhagen 1992) in response to ever-worsening news about stratospheric ozone levels [3]. Current controls are summarized in Table 1, but note that 'local' regulations more stringent than the Montreal Protocol agreements are being implemented [4]; for example, the EC phaseout deadline for CFCs is January 1, 1995.

The turn of the Montreal Protocol screw has been matched by a massive (and costly) industrial programme to develop and implement alternative compounds and technologies required to satisfy societal needs and consumer demands met by blacklisted compounds. Research and development (R&D) activities associated with chemically similar replacements for CFCs (e.g. CF_3CHCl_2 for $CFCl_3$; CF_3CH_2F for CF_2Cl_2) commenced in the late 1970s, well ahead of similar moves aimed at bringing replacements for 'Montreal' Halons to the marketplace [7].

Aided considerably by advances in the CFC replacements field, progress in the Halon area has accelerated remarkably since 1989 [7]. Several proposed acceptable halocarbon (i.e. chemically similar) alternatives for the Halon fire extinguishing agents 1301 (CF_3Br), 1211 (CF_2ClBr) and 2402 (CF_2BrCF_2Br) are currently being promoted commercially, and the main objective of this paper is to comment on the environmental and in-use characteristics of three front runners, namely HFCs (hydrofluorocarbons) 23 (CHF_3) and 227ea (CF_3CHFCF_3), and a blend of HCFCs (hydrochlorofluorocarbons) 22 (CHF_2Cl), 123 (CF_3CHCl_2) and 124 (CF_3CHFCl). Before proceeding with this task, it is necessary to set the scene regarding factors associated with the environmental acceptability of CFC and Halon

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*For Part 1, see ref. 1.

†See Appendix 1 for an explanation of halocarbon code numbers.

††Halon is a generic name usually associated in the past with a group of fire-extinguishing perhalogenated (i.e. fully halogenated) organic compounds analogous to CFCs (chlorofluorocarbons) but distinguished by the presence of bromine. This definition is adhered to throughout this article. Note, however, that when discussed within a strictly fire-fighting context, some authors refer to non-brominated compounds by Halon codes, e.g. CHF_2Cl = Halon 121, CF_3CHFCF_3 = Halon 37 (terminal zeros are omitted; see Appendix 1).

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TABLE 1. Current Montreal phaseout timetable for ozone-destroying anthropogenic halocarbons used dispersively (all years refer to January 1)

CFCs	(chlorofluorocarbons; e.g. $CFCl_3$, CF_2Cl_2, $CF_2ClCFCl_2$) 1994, 75% reduction[a], 1996, 100% phaseout
Halons	(bromofluoro- or bromochlorofluoro-carbons; e.g. CF_3Br, CF_2ClBr, CF_2BrCF_2Br) 1994, 100% phaseout
HCFCs	(hydrochlorofluorocarbons; e.g. CHF_2Cl, CF_3CHCl_2, CH_3CFCl_2) 1996, production freeze ('cap')[b] 2004, 35%; 2010, 65%; 2015, 90%; 2020, 99.5% reduction; 2030, 100% phaseout
HBFCs	(hydrobromofluorocarbons; e.g. CHF_2Br) 1996, 100% phaseout
CTC	(carbon tetrachloride, CCl_4) 1995, 85% reduction[c]; 1996, 100% phaseout
MC	(methyl chloroform, i.e. 1,1,1-trichloroethane, CH_3CCl_3) 1994, 50% reduction[c]; 1996, 100% phaseout
MB	(methyl bromide, CH_3Br) 1995, production freeze at 1991 levels; phaseout schedule not yet decided

[a] Based on 1986 production rates.

[b] Based on 1989 HCFC production figures plus 3.1% of 1989 CFC production [calculated on an ozone depletion potential (ODP)[d] weighted basis].

[c] Based on 1989 production figures.

[d] The efficiency of a halocarbon in depleting stratospheric ozone is commonly expressed in terms of an ODP value, which is specified relative to the depletion caused by the reference compound CFC-11 ($CFCl_3$) on a kg-for-kg basis [5]. Being a relative measure, this does not provide information about the absolute amount of ozone destruction, but does reveal the trade-off associated with replacement of one halocarbon by another [6].

substitutes of the halocarbon class. These are discussed briefly in the following section.

Assessment of environmental acceptability

Background

Judgements on the environmental acceptability of halogenated alternatives (known collectively as *fluorocarbons*, since they all contain carbon–fluorine bonds) to CFCs and Halons (fully-halogenated in both cases) demand the collection and evaluation of data concerning the following areas of impact: (i) the potential of the proposed alternatives to affect **both** stratospheric and tropospheric ozone (the troposphere extends roughly for the first 10–17 km from the Earth's surface, and the stratosphere through the next 30–40 km. Pressure and density decrease more or less exponentially with increasing altitude [5]); (ii) their potential to contribute to model-calculated global warming; and (iii) potential pollution caused by chemical degradation of alternatives in the atmosphere (alternatives are designed to suffer natural oxidation in the troposphere – see later).

Extensive scientific information bearing on these matters is continually being made available through independent research sponsored by the international AFEAS (Alternative Fluorocarbons Environmental Acceptability Study) Research Programme*. Health and safety aspects are being investigated through the Programme for Alternative Fluorocarbon Toxicity Testing (PAFT). AFEAS and PAFT activities are promoted by a large group of the world's chemical companies with the objective of hastening the provision of alternatives to CFCs via international cooperation with independent scientists, with government research programmes and among halocarbon producers.

Alternatives to CFCs (or analogous Halons) must have the correct physical, chemical and toxicological properties to make them suitable refrigerants, foam-blowing agents, aerosol propellants, solvents, etc. (or fire-extinguishants in the case of Halon substitutes) coupled with low ozone depletion potentials (ODPs). AFEAS Reports identify a number of partially-halogenated methanes, ethanes, and propanes which meet these criteria (see Table 2). By contrast with CFCs (or Halons), which can pass virtually unchanged to the stratosphere, these substitutes are degraded – at least partially – in the troposphere. Hence their atmospheric lifetimes are noticeably lower than those of the CFCs (or Halons) they are designed to replace [cf. CFC-11 ($CFCl_3$), 55 y; CFC-12 (CF_2Cl_2), 116 y; Halon 1301

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*The author was a scientific reviewer for the 1989 AFEAS Report [8] and continues to receive research results.

TABLE 2. Alternatives to CFCs[a]

Compounds		Tropospheric lifetimes, τ/y [9]	ODP[b]	GWP[c]
Hydrochlorofluorocarbons				
HCFC-22	CHF_2Cl	17.00	0.06	0.36
HCFC-123	CF_3CHCl_2	1.77	0.02	0.02
HCFC-124	CF_3CHFCl	7.28	0.02	0.10
HCFC-141b	CH_3CFCl_2	12.60	0.11	0.12
HCFC-142b	CH_3CF_2Cl	25.00	0.07	0.42
HCFC-225ca	$CF_3CF_2CHCl_2$	2.88	0.03	0.04
HCFC-225cb	CF_2ClCF_2CHFCl	8.59	0.03	0.15
Hydrofluorocarbons				
HFC-32	CH_2F_2	7.30	0[d]	0.13
HFC-125	CF_3CHF_2	40.70	0[d]	0.84
HFC-134a	CF_3CH_2F	15.70	0[d]	0.25
HFC-152a	CH_3CHF_2	1.80	0[d]	0.03

[a] Steady-state ODP and GWP (direct) values.

[b] By definition, ODP for CFC-11 ($CFCl_3$) = 1.0 (see footnote d, Table 1). Values taken from recent AFEAS literature.

[c] Normalised to that of CFC-11 ($CFCl_3$) on a mass-for-mass basis.

[d] See text.

(CF_3Br), 110 y]. Naturally this impacts favourably on values of both ozone depletion (ODPs) and greenhouse warming potentials (GWPs), so that all the compounds listed in Table 2 except HFC-125 meet up-coming requirements of the US Clean Air Act for ODP (<0.2) and Scandinavian standards for GWP (<0.5).

Note that at present all HFCs are assigned zero ODP values on the basis that they contain nether chlorine nor bromine. The effects on ozone concentrations, if any, of unchanged HFC material or tropospheric degradation products derived from HFCs reaching the stratosphere remain to be established.

The Achilles heel stratagem [1]

The rationale behind the choice of hydrohalocarbons (HCFCs, HFCs) to replace CFCs was simply that C–H bonds in organic molecules are susceptible to attack by hydroxyl 'free' radicals (HO·) present naturally in the Earth's troposphere. In effect, the troposphere is a low-temperature combustion system which acts as a chemical filter to restrict or even prevent contamination of the stratosphere by hydrogen-containing halocarbons, be they natural [e.g. methyl chloride or bromide (CH_3Cl or CH_3Br)] or man-made [methyl chloroform (CH_3CCl_3) or HCFC-22 (CHF_2Cl)]. The presence of at least one C–H bond is clearly a crucial molecular design feature for substitutes being groomed to replace CFCs or Halons. Too much hydrogen introduces a flammability-in-use factor, of course, as in the cases of HCFCs 141b and 142b (CH_3CFCl_2 and CH_3CF_2Cl) and HFC-152a (CH_3CHF_2). CFC or Halon substitutes containing abstractable hydrogens are referred to as 'tropospherically soft', as distinct from 'tropospherically hard' ozone depleters such as CFC-12 (CF_2Cl_2) and Halon 1301 (CF_3Br); the only significant natural removal process for the 'hard' types, of course, is transport to and subsequent photolysis in the stratosphere.

Decomposition of HCFCs/HFCs initiated by hydroxyl radical attack is well exemplified in the following discussion of the Halon alternatives chosen for review. Readers seeking more extensive background information should consult refs. 1 and 5; ref. 10 contains a detailed examination of the relationships between C–H bond strengths, activation energies for removal of hydrogen by hydroxyl radicals ($C{-}H + HO\cdot \rightarrow C\cdot + H_2O$), tropospheric lifetimes (τ) and ODP values. In brief, the relative ease with which a hydroxyl radical can abstract hydrogen from a C–H bond depends crucially on the molecular environment of that C–H bond; tropospheric lifetimes decrease as the rate of abstraction increases, but even quite reactive HCFCs still contribute to stratospheric ozone depletion by chlorine [2%–15% of the chlorine content of HCFCs with intermediate lifetimes (1–22 y) is released in the stratosphere] [2b]. Note that large uncertainties in estimated tropospheric HO· concentration dominate the absolute uncertainty of lifetimes (τ) of HCFCs/HFCs, rendering the absolute values of ODPs uncertain by as much as a factor of two [6]. However, the relative values of lifetimes and hence relative ODPs (and GWPs) depend not on absolute natural HO· abundance but on relative rate constants for H abstraction by HO· from HCFCs/HFCs. A large body of kinetic data for such reactions is now available from laboratory studies, and values are constantly being refined; accuracies seem to fall in the 10%–30% range [6]. For bromine-containing compounds [HBFCs], current uncertainties regarding lifetimes are significant [6].

Considerable uncertainties existed until relatively recently concerning degradation pathways for CFC substitutes post-abstraction of hydrogen by hydroxyl radical [1, 8]. Much has been done since 1989 to remedy this situation, and the discussion of degradation mechanisms in the remainder of this paper relates to results achieved through AFEAS sponsorship [11–13]. Part 3 of this series of papers will contain considerably more information.

Chemically similar ('in-kind') replacements for Halon FE (Fire Extinguishing) agents

Introduction [14–16]

All commercially significant CFCs are non-flammable and possess some degree of fire-extinguishing ability, but their bromine-containing analogues are outstanding in this respect [17].

The original bromocarbon fire extinguishants (FEs) were methyl bromide (MB; bromomethane, CH_3Br) and its monochloro derivative [CBM; bromochloromethane, CH_2ClBr (often referred to as CB)]. These two were used for military purposes during World War II to supplement the well-established FE carbon tetrachloride [CTC; tetrachloromethane, CCl_4]. The realisation that delivery of bromine to a fire by these compounds enhances the chemical mechanisms of extinction (extinction involves interference with the complex free-radical chain mechanisms of combustion reactions; the effectiveness of the halogens as combustion inhibitors decreases in the order of decreasing atomic number (iodine > bromine > chlorine > fluorine) [14]) achieved with CTC prompted a search for less toxic brominated agents. The very low toxicities of perfluorocarbons and CFCs, coupled with the well-known ability of fluorine substituents to confer volatility, pointed the way to the simple bromofluorocarbons CF_3Br [bromotrifluoromethane, BTM), CF_2Br_2 [dibromodifluoromethane] and CF_2BrCF_2Br [1,2-dibromotetrafluoroethane, DTE; Fluobrene®] and the bromochlorofluorocarbon CF_2ClBr [bromochlorodifluoromethane, BCF®], which are now known as FEs 1301, 1202, 2402 and 1211, respectively, according to the Halon code*.

Halons 1301, 1211 and (to a lesser extent) 2402 subsequently became seemingly indispensable worldwide in fire-protection systems for all manner of civil, commercial, military and industrial devices, installations and property. Unfortunately, these three Halons – like CFCs – are tropospherically hard, so material emitted to the Earth's atmosphere during discharge testing, servicing/filling of systems, training exercises or actual fire-fighting (and also accidentally) is transported essentially unchanged to the stratosphere, where C–Br bonds are photolysed, releasing bromine atoms. Indeed, some 30% of the 1986 world production of Halon 1301 is estimated to have been released to the atmosphere [7]. On an atom-for-atom basis, bromine has been identified as a far more effective (*c.* 40 times [6]) than chlorine as an 'ozone destroyer' – as reflected by computed steady-state polar ODP values [CF_3Br, 12.5; CF_2ClBr, 4.1; CF_2BrCF_2Br, 5.9 ($CFCl_3 = 1.0$ by definition)] [6]†. This factor resulted in the inclusion of tropospherically-hard Halons in the original version (1987) of the Montreal Protocol, despite the distinction that these brominated compounds constituted only a small fraction of the total annual consumption of CFCs [7]. Thus, Halons 1301 and 1211 are thought to account for only about 12% of all brominated source gases in the troposphere [18]. Tropospherically soft methyl bromide (ODP 0.57), an important soil fumigant, seems to be the most abundant organobromine component of the atmosphere, but man-made material accounts for only 25% ± 10% of all releases since massive quantities (est. 300,000 tonnes p.a.) arise from natural sources (oceans, volcanoes) [19].

Identifying Halon replacements

Naturally, the so-called Achilles heel stratagem (see above) involved in the development of HCFC and HFC replacements for CFCs was adopted immediately in the search for environmentally friendly 'in-kind' replacements for Halons. And with bromine's ability to confer effective combustion suppression in mind, producers fairly quickly identified HBFCs 22B1 and 124B1 [bromodifluoromethane; CHF_2Br (Great Lakes)] and [2-bromo-1,1,1,2-tetrafluoroethane; CF_3CHFBr (ICI)] as potential replacements.

In terms of physical properties, toxicity and extinguishing performance, HBFC-124B1 rates as a satisfactory 'drop-in' replacement for Halon 1211 (CF_2BrCl). ['Drop-in' replacements for Halons (or CFCs) utilise the same equipment and retain the unique combination of properties of the substances being substituted.] Indeed, it seems to meet all ICI's own criteria, but the compound's ozone depletion potential (0.3 [7])* does not comply with the US government's Clean Air Act ruling that the release of chemicals with an ODP greater than 0.2 should be banned by the year 2000 [21]. For this reason, ICI's work on this otherwise attractive Halon replacement has been discontinued [7].

The same problem arises with HBFC-22B1 (lowest-value estimated ODP = 0.19 [7]), which the Great Lakes Chemical Corporation introduced as Firemaster™ 100 (FM-100) to replace both Halon 1301 and 1211. More recently, HBFC-133B1 (CF_3CH_2Br: atmospheric lifetime 4.1 y) has come under scrutiny, but its computed ODP is unacceptable (0.84, with an overall uncertainty factor of about two) [18].

The recognised high efficiency of the bromine-catalysed destruction of ozone (on an atom-for-atom basis, Br· is believed to be 30–100 times more effective than Cl·) led Aerodyne researchers to conclude recently that if so-called hydrogenated Halons are to replace their fully-halogenated analogues, troposphere lifetimes of the order of only a few months will probably be necessary to permit widespread use of these compounds [18]. Du Pont seemingly adopted the viewpoint that brominated products are inappropriate alternatives to Halons some time ago [22], and, like Great Lakes,

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*The numbers correspond successively (left to right) to the number of atoms of carbon, fluorine, chlorine, bromine and iodine present per molecule, terminal zeros being omitted (see Appendix 1).

†See footnote d, Table 1.

*Tickell in his article 'What Future for Halons' [20] quotes an ODP range of 0.3–0.5 (tropospheric lifetime, τ, 3.9 y) and comments on the validity of current comparisons between bromine and chlorine ODPs (see also ref. 6).

have invested in the development of HCFCs and HFCs as Halon replacements with the objective of achieving low ODP values with minimal loss of extinguishing characteristics.

Currently, Du Pont are offering HFC-23 [FE-13; trifluoromethane (trivial name fluoroform), CHF_3] and North American Fire Guardian a blend of HCFCs 22 (CHF_2Cl), 123 (CF_3CHCl_2) and 124 (CF_3CHFCl) [NAF SIII] as viable alternatives to Halon 1301 (CF_3Br), while Great Lakes are promoting HFC-227ea [FM-200; 1,1,1,2,3,3,3-heptafluoropropane (or, more succinctly, 2*H*-heptafluoropropane), CF_3CHFCF_3]*. Each of these is discussed below from the viewpoints of their 'in-use' chemistry and the potential impact of releases on the environment. The latter aspect is directly related to the author's long-standing concern about 'in-kind' CFC replacements [1, 23].

HFC-23 (FE-13™)

As a fire extinguishant

As a flame extinguishant, HFC-23 (CHF_3, b.p. −82.03 °C) is about 25% as effective as Halon 1301. Its physical properties (high vapour pressure; low liquid density) prevent its use in existing Halon 1301 equipment, but is appears to offer possibilities as a drop-in replacement for carbon dioxide [7]. Already established commercially as a low-temperature refrigerant in Du Pont's Freon range, HFC-23 has a low inhalation toxicity [$LC_{50} > 65$ vol.% (rat; 4-h exposure)] and does not cause cardiac sensitisation in animals at concentrations up to 80 vol.% in air [7].

Interestingly, HFC-23 is produced, amongst other species, when Halon 1301 is added to hydrocarbon flames, e.g. $CF_3Br + CH_4(\text{flame}) \rightarrow CHF_3$, $CH_2{=}CF_2$, COF_2, HF, CH_3Br, HBr, Br_2 [24]. The bromine abstraction reaction, $CF_3Br + H\cdot \rightarrow CF_3\cdot + HBr$, seems to be responsible for 90% of the disappearance of the flame inhibitor; subsequent attack on hydrogen-containing flame components (HX) by trifluoromethyl radicals thus released from the Halon (or by simple pyrolysis, $CF_3Br \rightarrow CF_3\cdot + Br\cdot$) appears to be the major source of HFC-23: $CF_3\cdot + XH \rightarrow X\cdot + CHF_3$ (e.g. HX = hydrocarbon, H_2, HBr, H_2O) [24]. HFC-23 thus formed *in situ* can be lost in several ways, including thermal dehydrofluorination ($CHF_3 \rightarrow CF_2 + HF$); these impact on flame-inhibition mechanisms and throw light on the somewhat greater efficiency of CF_3Br as a fire-fighting agent than expected on the basis of its bromine content [24].

The halogens contained in Halons (CF_3Br, CF_2ClBr) appear mainly as hydrogen halides in the breakdown products derived from flame inhibition under test conditions; only relatively small amounts of free chlorine and/or bromine are normally detected, and carbonyl halides (COXY; X, Y = F, Cl, Br) usually appear only when oxygen is in short supply [7]. Water, generated by combustion or present in ambient air, can hydrolyse carbonyl halides to carbon dioxide and hydrogen halides.

Hydrogen fluoride (HF) and carbonyl fluoride (COF_2) will be generated when HFC-23 is used to control fires. As with the Halons [7], no free fluorine (the most reactive of the chemical elements) should be encountered. Production of hydrogen fluoride, a notorious substance [25], in unacceptable amounts presumably may occur under some circumstances (the author has seen no test data yet).

In tests on human volunteers [26], hydrogen fluoride gas [known as AHF – anhydrous hydrogen fluoride (b.p. 19.54 °C) – to distinguish it from hydrofluoric acid, its solution in water] at a concentration in air of 32 ppm is reported to have been tolerated for 3 min, although a flat sour taste and mild sensory irritation of the eyes, nose and upper respiratory tracts were apparent [26]. Sensory irritation was more pronounced when the concentration was approximately doubled (61 ppm), and was marked at 122 ppm, with additional 'smarting' of the skin. Skin contact with AHF or hydrofluoric acid produces painful burns which require special medical treatment [25]; decontamination procedures following fire extinguishment with HFC-23 will need to allow for this hazard, particularly when large fires are involved.

Atmospheric chemistry

Atmospheric chemistry models use mathematical expressions to describe the chemical reaction rates, transport and ultraviolet photolytic processes which determine the chemical fates of volatile halocarbons entering the Earth's atmosphere at ground level. Natural degradation of an airborne halocarbon occurs primarily through one or more of the following homogeneous processes [27]: reaction with the hydroxyl radical ($HO\cdot$) in the troposphere or the stratosphere, reaction with electronically-exited oxygen atoms [$O(^1D)$] in the stratosphere and UV photolysis (photochemical degradation)

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*The numerical code for a fluorinated propane is derived according to standard rules (see Appendix 1). However, two alphabetical suffixes (as distinct from one in the case of an ethane) are required to pinpoint the isomer under discussion, the first of which defines the substituents present on the central carbon atom (C-2); priority is assigned according to the sum of the atomic weights of the substituents (cf. Appendix 1), thus CCl_2 = a, CFCl = b, CF_2 = c, CHCl = d, CHF = e and CH_2 = f. The second alphabetical suffix defines the substituents at the flanking carbons (C-1 and C-3) and is identified in exactly the same way as for the analogous two-carbon molecule, i.e. an ethane (see Appendix 1). Thus, CF_3CHFCF_3 (ethane) equivalent CF_3CF_3) is 227ea, while the only other isomer $CF_3CF_2CHF_2$, is 227cb.

in the stratosphere*. In-kind substitutes for Halons or CFCs are normally designed to be vulnerable to attack by hydroxyl radicals (abstraction of hydrogen atoms from C−H bonds — see above); this results in atmospheric lifetimes significantly shorter than those of the fully halogenated compounds they are intended to replace. Clearly a balance has to be struck between achieving a tropospheric lifetime so short that unacceptable levels of local pollution are created in the vicinity of releases (urban 'smog' — which would involve photochemical ozone production [5, 28]), and one so long that it allows too great a proportion of released material to enter the stratosphere and possibly participate in thinning of the ozone layer. HFC-23, with a calculated tropospheric lifetime ranging from 310 to 635 y, depending on the method used [29] (average = 411 y), falls into the latter category with a vengeance!

Uncertainty exists at present regarding the fate of HFC-23 entering the stratosphere. Presumably, photolytic decomposition will not be important up to the top of the stratosphere, as believed to be the case for HFC-134a (CF_3CH_2F), for example [30]. Chemical decomposition (hydrogen-abstraction reactions) involving hydroxyl radicals or excited-state oxygen atoms (and presumably chlorine atoms [31]) would proceed, yielding the trifluoromethyl radical, $CF_3\cdot$, the potential of which to destroy ozone is mentioned later, but this would be too slow to prevent HFC-23 releases accumulating and hence making an unwelcome contribution to greenhouse warming of the Earth's surface.

HCFC blend NAF SIII

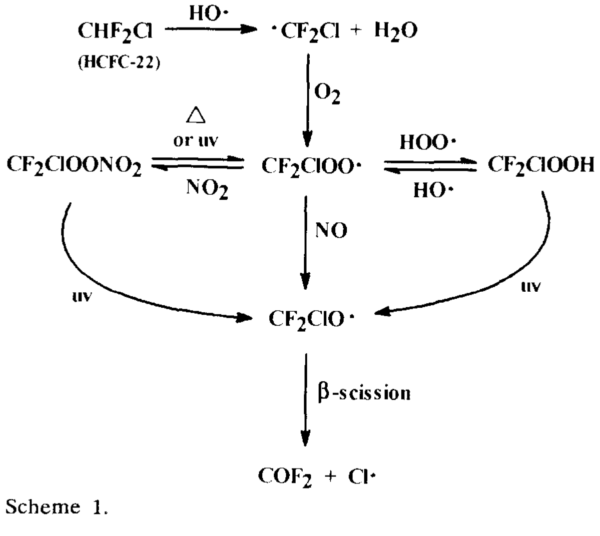
Atmospheric considerations

The North American Fire Guardian blend NAF SIII (b.p. −38 °C) comprises HCFC-22 (CHF_2Cl, b.p. −40.8 °C) blended with small amounts of HCFC-123 (CF_3CHCl_2, b.p. 27.8 °C) and HCFC-124 (CF_3CHFCl, b.p. −12 °C) plus a hydrocarbon stabiliser. The major (82%) component has the longest estimated (total) atmospheric lifetime (τ_{Net}†) (CHF_2Cl 15.8; CF_3CHCl_2 1.7; CF_3CHFCl 6.9 y) [9].

Purported to be a drop-in replacement for Halon 1301, the toxicity of NAF SIII is slightly higher than that of Halon 1301 but lower than that of 1211. Its steady-state ODP is substantially lower than that of Halon 1301 (0.044 versus 12.5) and, correspondingly, the GWP is less than one-third of that of CFC-11 (CHF_2Cl, 0.36; CF_3CHCl_2, 0.02; CF_3CHFCl, 0.10). Nevertheless, HCFC-22 (the major component) and its congeners are all viewed as undesirable for any dispersive application; indeed EC concern about HCFCs has resulted in the adoption of the year 2014 as the phaseout date for compounds of this class. In this context, note the recent argument [6] that long-term ODPs (based on steady-state atmospheric impact) are not appropriate for making shorter-term forecasts (cf., for example, $ODP_{HCFC\text{-}22} = 0.14$ at 20 y, decreasing to 0.05 at 500 y).

Experimental studies [32] have shown that tropospheric degradation of HCFC-22 leads to the production of carbonyl fluoride, COF_2, and chlorine atom (see Scheme 1). The end products are therefore carbon dioxide, hydrofluoric acid (via hydrolysis of COF_2 by atmospheric moisture) and hydrochloric acid ($Cl\cdot + CH_4 \rightarrow HCl + CH_3\cdot$, etc.). Although the ultimate halogen-containing breakdown products are acidic compounds, their contribution to acid rain is rated in AFEAS literature as 'insignificant'.

Radical-initiated breakdown by HO· of HCFC-123 and HCFC-124 give rise to the acid halides CF_3COCl and CF_3COF, respectively, and hence trifluoroacetic acid can be formed (see Scheme 2 relating to the tropospheric conversion of HCFCs 123 (X = Cl) and 124 (X = F to trifluoroacetic acid [1, 33–35]) in addition to hydrohalic acids. Contamination of rain and hence groundwater by trifluoroacetic acid produced from two-carbon in-kind CFC replacements (including HFC-134a [1, 36], the primary replacement at present for refrigerant CFC-12) is of some concern, and the matter is being addressed through AFEAS-sponsored work on potential interactions of the acid with the biological environment [12, 37]. At present, AFEAS maintains that even if hundreds of thousands of tonnes of the 'new fluorocarbons' (such as HFCs 22 and HCFCs 123 and 124) were to be released each year, they would



Scheme 1.

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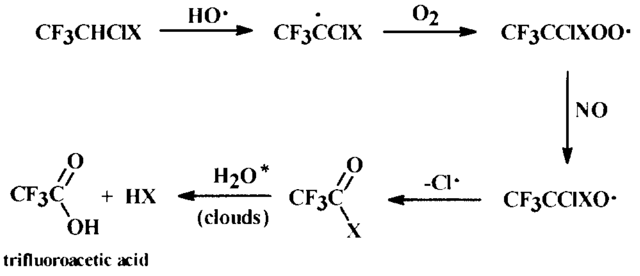
*Hydroxyl radicals [derived thus: $O_3 + UV$ (≤310 nm) light $\rightarrow O^* + O_2$; $O^* + H_2O \rightarrow HO\cdot + HO\cdot$ and $O^* + CH_4 \rightarrow CH_3\cdot + HO\cdot$] dominate the daytime chemistry of the troposphere in the same manner that ozone and oxygen atoms dominate stratospheric chemistry [$O^* = O(^1D)$] [5].

†$1/\tau_{Net} = 1/\tau_{Trop} + 1/\tau_{Strat}$. Note that τ_{Trop} for HCFC-22 = 17.0 y, and $\tau_{Strat} = 240$ y [9].



(X = F or Cl)

Scheme 2. *Note that UV photolysis of CF_3COCl will compete with hydrolysis as a removal process.
cf. Scheme 1 for details of the first three steps.

not contribute appreciably to the natural chloride (Cl^-) or fluoride (F^-) burden of the biosphere. Any trifluoroacetic acid formed, it is maintained, will be present at such low concentrations in rain or sea water (parts per billion or less) that adverse effects are not expected. Concern regarding bioaccumulation and biotransformation (possibly to the very well known mammalian poison monofluoroacetic acid, CH_2FCO_2H) of HCFC/HFC-derived trifluoroacetic acid remains to be allayed [38].

In-use decomposition

Extinguishment of fires with NAF SIII clearly will produce mainly hydrogen halides (HCl, HF) and carbonyl halides (COF_2, COFCl), together with traces of two-carbon species from the minor constituents (CF_3COF, CF_3COCl). The author has seen no detailed test data yet.

The 'chlorine problem'

A major drawback to the adoption of in-kind CFC or Halon substitutes of the HCFC class (e.g. NAF SIII) is the uncertain future facing all chlorine-based chemicals [39].

EC phaseout targets for HCFCs are more stringent than those contained in the current Montreal Protocol (see Table 1). The Commission on the EC Environment Ministry's ozone protection measures recently proposed a cap on HCFC consumption of 2.5% (i.e. 2.5% of CFC and 100% of HCFC consumption of ODP tonnes in 1989) and their phaseout by the year 2015 [40]. (This equates to about 15 000 tonnes of HCFCs less than the 3.1% cap under the Montreal Protocol.)

Measurements by instruments aboard NASA's upper atmospheric research satellite have revealed quite recently that depletion of stratospheric ozone by chlorine is of greater concern than previously thought [41]. Presumably such information will impact significantly on current phaseout timetables for HCFCs, making substitutes of this class even less attractive commercially for dispersive applications.

HFC-227ea (FM-200™)

2*H*-Heptafluoropropane (CF_3CHFCF_3, HFC-227ea), b.p. −16.4 °C, is one of several HFCs specified in a recent Great Lakes patent entitled 'Fire extinguishing methods and blends utilizing hydrofluorocarbons' [42]. When used alone, it is known commercially as FM-200™. Although HFC-227ea clearly does not contain chlorine (unlike NAF SIII™), its manufacture involves chlorinated intermediates, as does that of HFC-23 (CHF_3, FE-13); naturally, the use and almost certain emission of ozone-depleting substances during the production of HFCs is a fact of life which has not escaped the attention of environmental activists like Greenpeace.

The extinguishing characteristics of HFC-227ea are described in an informative report available from Great Lakes entitled 'FM-200™, The First Choice in Environmentally Superior Fire Protection'. In short, the test concentration requirement for HFC-227ea (5.8 vol.% in air) is about twice that for Halon 1301; existing Halon-type equipment seemingly can be adapted; and the 4-h LC_{50} value (rat) for the HFC exceeds that of Halon 1301.

The Great Lakes report makes only brief mention of decomposition products derived from FM-200 during flame suppression; and the possibility of stratospheric ozone depletion by releases of FM-200 is dismissed since the agent contains neither chlorine nor bromine. Each of these matters is discussed below.

In-use decomposition of HFC-227ea

Detailed information on the decomposition products (complete list of identities, relative amounts) produced in real-life fires appears not to have been released yet. The Great Lakes report informs potential users that "some small amount of the Halon decomposes to form halogen acids" during fire suppression with Halon 1301 (HBr principally and HF)* but "the very sharp, acidic odour of these products serves as an effective warning to the user well before any hazardous threshold is reached". After pointing out that FM-200™ contains no bromine, the report continues "However tests show that for all non-brominated agents, hydrofluoric acid† can form in larger quantities upon exposure of the agent to the flame front. Hydrofluoric acid quantities can be minimized and maintained at safe levels by use of rapid detection and discharge of the agent within recommended guidelines." Thermal production of HF from FM-200™ is inevitable, given its molecular struc-

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*The concentration of HF (hydrogen fluoride) usually is less than that of the other hydrogen halide(s). For example, the recent HMSO Halon booklet [7] gives details of extinguishment of a heptane fire with Halon 1211 (CF_2ClBr) which produced (HCl + HBr), HF and (Cl_2 + Br_2) in concentrations of 50, 10 and 2 ppm ($COCl_2$ 'not detected', i.e. <0.25 ppm).

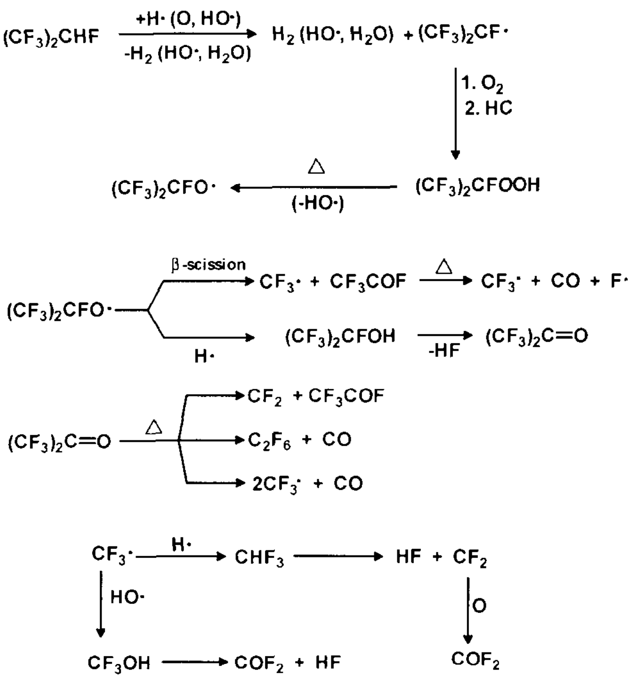
†Meaning hydrogen fluoride.

ture, and it seems clear that when large fires are involved safety limits may be exceeded. This 'HF problem' also arises with FE-13. Simple monitoring of test chamber atmospheres using mice is mentioned in ref. 42.

In a limited ICI laboratory investigation of HFC-227ea as an extinguishing agent [43], the organic compounds detected by GC–MS in exit gas from a mini cup-burner apparatus (n-heptane flame) included tetrafluoroethene, pentafluoroethane, hexafluoroethane and hexafluoropropene. The notoriously toxic gas octafluoroisobutene [$(CF_3)_2C{=}CF_2$, perfluoroisobutene (PFIB)] was not detected; however, the limit of detection was only *c.* 10 ppm – which is significantly greater than the normal accepted hygiene standard of 0.01 ppm. It should be noted that single exposures of rats to as little as 0.50 ppm are lethal [44]. Reference 44 contains information on the deaths of two out of five humans accidentally exposed to a gas containing 2% PFIB. The recommended occupational exposure limit for PFIB is 10 ppb [45]. Clearly, further experimentation is required to resolve the important question of whether PFIB can be produced in real-fire situations [e.g. via $CF_3CF{=}CF_2 + CF_2 \rightarrow (CF_3)_2C{=}CF_2$]*. Inorganic products (monitored by FT-IR spectroscopy) were found to be carbon monoxide, carbon dioxide, carbonyl fluoride and hydrogen fluoride, produced in the molar ratio of 1.5 (CO):14 (CO_2):3.8 (COF_2):20 (HF) [43].

From a theoretical viewpoint, flame inhibition with HFC-227ea is expected to produce at least hydrogen fluoride, carbonyl fluoride, hexafluoropropene and (initially) trifluoroacetyl fluoride and hexafluoroacetone (see Scheme 3). Hexafluoropropene, generated mainly, or even exclusively, via thermal dehydrofluorination of HFC-227ea ($CF_3CHFCF_3 \rightarrow CF_3CF{=}CF_2 + HF$) is an obvious precursor of fluorocarbonyl compounds, e.g. $CF_3CF{=}CF_2 + O \rightarrow CF_3COF + CF_2$ followed by $CF_2 + O$ (or $HO\cdot$) $\rightarrow COF_2$ (or $COF_2 + H\cdot$) [47]. Presumably, however, acid fluorides and hydrogen fluoride may also arise from flame-inhibiting processes based on the abstraction of the hydrogen atom from HFC-227ea (Scheme 3). Hydrolysis of fluorocarbonyl halides ($CF_3COF + H_2O \rightarrow CF_3CO_2H + HF$; $COF_2 + 2H_2O \rightarrow CO_2 + 2HF$) and of any perfluoroisobutene [$(CF_3)_2C{=}CF_2 + 2H_2O \rightarrow (CF_3)_2CHCO_2H + 2HF$] by water produced during the combustion of hydrocarbon material or present in ambient air will be secondary sources of HF.

Clearly, determination of the complete microstructure of hydrocarbon–oxygen flames undergoing suppression by HFC-227ea will prove to be a demanding exercise. It will be interesting to determine the role played by the olefin hexafluoropropene, a well-known commercial monomer (known as HFP) used in the production of important fluoropolymers. A recent review of the toxicology of fluorine-containing monomers contains extensive animal data on HFP, the conclusion being that it is not very toxic on an acute basis [LC_{50} (rat; 4-h exp.) approximately 3000 ppm] [44]. Acute exposure to HFP is irritating to the lung and respiratory tract and can cause kidney injury at relatively high concentrations (>400 ppm) [44]. Hexafluoroacetone (HFA; CF_3COCF_3), a likely decomposition product (see Scheme 3), is only 'moderately toxic' by inhalation [LC_{50} (rat; 4-h exp.) 300–400 ppm] [44].



HC = hydrocarbon material

Scheme 3.

Atmospheric chemistry

By ignoring tropospheric photolysis (confidently expected to be negligible), stratospheric photolysis (not significant, by analogy with other HFCs) and attack by excited-state oxygen atoms [$O(^1D)$ – again expected to be slow], the atmospheric lifetime of HFC-227ea has been estimated to be 42 y by Aerodyne scientists, based on kinetics determined experimentally for hydrogen abstraction by hydroxyl radical [18]. Great Lakes quote an atmospheric lifetime of 31-42 years [48] and a greenhouse warming potential of 0.3–0.6 (CFC-11 = 1.0), the upper value falling outside the acceptable Scandinavian upper limit (0.5)*. Interestingly, calcu-

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*Note that PFIB is known to be produced via pyrolysis of hexafluoropropene [46a], hexafluoroacetone [46b] or tetrafluoroethylene [46c].

*Personal communication from Dr R.L. Powell (ICI). According to the Swedish Refrigeration Standard, Fact Sheet 6, HFC refrigerants with a GWP greater than 0.5 and/or an ODP greater than 0.1 may only be used under exceptional circumstances.

lations based on empirical structure–activity relations for attack by $HO\cdot$ on HFCs give tropospheric lifetimes of 63 (ab initio method) and 72 y (semi-empirical calculation) for HFC-227ea [49]. Both sources of information assume that HFC-227ea has zero potential to destroy ozone (ODP = 0; CFC-11 = 1.0) based on the fact that it can carry neither chlorine nor bromine to the stratosphere.

As happened with HFCs and HCFCs in the past, the existing data relating to the atmospheric lifetime of HFC-227ea, and hence GWP, will be checked and refined. From the information presently available, it is clear that HFC-227ea possesses too long a tropospheric lifetime (i.e. resistance to attack by $HO\cdot$) and hence GWP to make it a welcome addition to the present-day atmospheric burden of organohalogen compounds.

Assessment of the environmental acceptability of HFC-227ea also requires that experimental information be available concerning the actual pathways (mechanisms) by which the atmosphere will cleanse itself of releases. None seems to have been published as yet. From a consideration of the results reported so far for other in-kind replacements for CFCs and Halons [11–13, 50] (see Schemes 1 and 2), it is reasonable to expect that trifluoroacetyl fluoride and trifluoromethyl radical will be generated via fragmentation of the alkoxy radical, $(CF_3)_2CFO\cdot$, formed by hydroxyl radical attack: $(CF_3)_2CHF + HO\cdot \rightarrow (CF_3)_2CF\cdot \rightarrow$ (with O_2) $(CF_3)_2CFOO\cdot \rightarrow$ (with NO, etc., cf. Scheme 1) $(CF_3)_2CFO\cdot \rightarrow$ (β-scission) $CF_3\cdot + CF_3COF$. The acid fluoride would be a tropospheric source of trifluoroacetic acid and hydrofluoric acid [CF_3COF + water $\rightarrow$ CF_3CO_2H(aq.) + HF(aq.); see Scheme 2]; in the upper stratosphere, its photochemical decomposition ($CF_3COF \rightarrow \rightarrow CF_3\cdot + CO + F\cdot$) might have an impact on ozone depletion.

Investigations of the fate of $CF_3\cdot$ radicals, and of the related alkoxy radicals $CF_3O\cdot$ [$CF_3\cdot + O_2 \rightarrow CF_3OO\cdot \rightarrow$ (with NO) $CF_3O\cdot + NO_2$ (cf. Scheme 1)] are progressing [51]. Results so far indicate that the major fate of $CF_3O\cdot$ radicals will involve reaction with hydrocarbons (e.g. $CH_4 + CF_3O\cdot \rightarrow CH_3\cdot + CF_3OH$; $CF_3OH \rightarrow COF_2 + HF$) [52]. In the stratosphere, it appears that ozone removal via a chain reaction involving the step $CF_3O\cdot + O_3 \rightarrow CF_3OO\cdot + O_2$ is a minor possibility.

This subject and the environmental fate of the potential atmospheric degradation product trifluoroacetic acid is deferred to Part 3 of this series of reviews, which will cover published data on the tropospheric fates of 'in-kind' CFC substitutes such as HFC−134a (CF_3CH_2F) and HCFCs 123 (CF_3CHCl_2) and 124 (CF_3CHFCl).

Acknowledgment

I am greatly indebted to Dr H.M. Deger (Hoechst) for bringing ref. 43 to my attention and providing a copy. He has also informed me that simulated tropospheric oxidation of HFC-227ea gives CF_3COF and COF_2 (work done by Professor R. Zellner's group in Essen).

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Appendix 1. Numerical codes for fluorocarbons

Numerical codes for designating the simple fluorocarbons have been in use for many years. The international system used today was officially adopted on 3 June, 1957, as Standard 34 of the American Society of Heating, Refrigeration and Air-Conditioning Engineers (ASHRAE) [53]. It is a system originating from Du Pont USA, and although other CFC producers initially invented their own codes, the ASHRAE system replaced them some time ago.

Reading a CFC code number from right to left, the first digit defines the number of fluorine atoms; the second is the number of hydrogens plus one; and the third is the number of carbon atoms minus one. The third number is omitted is zero, e.g. CF_2Cl_2 is coded 12 not 012, and CHF_2Cl is 22 not 022. Note that the number of chlorines follows from the knowledge that the valency of carbon is four, i.e. the number of chlorines is found by subtracting the sum of the fluorine and hydrogen atoms from the total of atoms which can be connected to the carbon atoms. When no chlorine is present, the compound can be an HFC (hydrofluorocarbon; e.g. CH_2F_2, coded 32, CHF_3, coded 23) or a PFC (perfluorocarbon; e.g. CF_4, coded 14).

Thus, use of only two numerals reveals immediately that a methane (CH_4) derivative is involved. Moving to ethanes, the well-known phenomenon of constitutional (positional) isomerism complicates matters. There is no problem with chloropentafluoroethane, CF_3CF_2Cl (CFC-115, i.e. 5 fluorines, 0 hydrogens + 1, and 2 carbons − 1), but dichlorotetrafluoroethane ($C_2Cl_2F_4$) has two possible structures, namely CF_2ClCF_2Cl and CF_3CFCl_2. The former is coded CFC-114 and the latter CFC-114a, according to the ASHRAE sub-rule that when isomers exist [i.e. compounds which have identical molecular formulae but different molecular structures (and hence properties)], the most symmetrical one takes precedence over the others, which are allocated alphabetical suffixes (a, b, c...) as they become more unsymmetrical. Symmetry is determined by adding together the atomic weights of the substituents (H = 1, F = 19, Cl = 35.5) attached to each carbon and subtracting one sum from the other. For example, with the well-known solvent CFC-113 ($CF_2ClCFCl_2$), the difference is $(19+2\times35.5)-(2\times19+35.5)$, i.e. 16.5, which is less than that (49.5) for its isomer CF_3CCl_3, hence the latter is CFC-113a. Likewise CF_3CH_2F is HFC-134a, the obviously more symmetrical isomer CHF_2CHF_2 being HFC-134. The HCFC $C_2H_3Cl_2F$ has three isomers, $CH_2ClCHFCl$, CH_2FCHCl_2 and CH_3CFCl_2 coded 141, 141a and 141b, respectively.

The fire-extinguishing industry uses a numbering system (Halon FE code) for bromofluorocarbons or bromochlorofluorocarbons which reveals, reading from left to right, the number of carbon, fluorine, chlorine and bromine atoms respectively in each molecule, e.g. CF_3Br is Halon FE-1301, CF_2ClBr is Halon FE-1211 and CF_2BrCF_2Br is Halon FE-2402 [7]. The CFC code system has been extended to apply to such brominated compounds. Here the letter B is placed after the designation for the code indicating the number of carbon, hydrogen and fluorine atoms, followed by a numeral defining just how may bromine atoms are present. Thus, CF_3Br is BFC-13B1, CF_2ClBr is BCFC-12B1 and CF_2BrCF_2Br is BFC-114B2.

For more information, see ref. 16. Propane nomenclature is explained in the main text, i.e. where HFC-227ea (CF_3CHFCF_3) is discussed.