Chapter 7: SEARCH FOR NEW FIRE SUPPRESSANT CHEMICALS

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7.1 FIRE SUPPRESSANT REPLACEMENT KNOWLEDGE PRIOR TO THE NGP

7.1.1 Overview of Early Halon Replacement Efforts

As described in Chapter 1 of this book, in the years following the Army-Purdue study, there was extensive scientific and engineering research that led to the commercialization and widespread use of halon 1301. Following the adoption of the Montreal Protocol on Substances That Deplete the Ozone Layer in 1987, organized efforts to identify replacements were initiated by a broad range of governmental and non-governmental groups. These efforts were hastened in the United States by the planned phase-out of production of halon 1301 (CF_3Br) and halon 1211 (CF_2ClBr) by the end of 1993.

The replacement of halon 1301 presented some daunting challenges. Halon 1301 is unique as a brominated halocarbon. Its -58 °C boiling point is the lowest of the bromofluoroalkane chemical family, and its toxicity is quite low. It is an efficient fire suppressant and explosion inertant. It has great dimensionality (space filling), high tolerance to less than optimal discharge technique, and excellent chemical stability. Early results showed that a small change in the molecule could lead to large and conflicting effects on key performance properties. For example, the replacement of a fluorine atom by a hydrogen atom to produce halon 1201 (CF_2HBr) reduced the estimated atmospheric lifetime from 65 years to 15 years, but raised the boiling point to -15 °C.

Nonetheless, the search for alternatives to the firefighting halons began as a quest for a "drop-in," a chemical that would fit into existing fire suppression systems and perform just like or better than the halon it was replacing. During the early years of this research, there were frequent changes in thinking among those involved in identifying new chemicals. For instance, it was realized that instead of a single drop-in replacement being identified for halon 1301 (as well as halon 1211) the world of fire suppression applications was going to see a broad range of new agents and technologies. Furthermore, the criteria for environmental acceptability changed. With the emphasis on dramatic reductions in both stratospheric ozone depletion effects and atmospheric global warming potentials, the research focus shifted to identifying short atmospheric lifetime molecules. These compounds incorporate structural components that are reactive with atmospheric constituents of the atmosphere or are photochemically reactive, as shown in Table 7–1.

Table 7–1. Tropospheric Removal Mechanisms.

Primary Removal Mechanism	Example Families
Photodegradation	Iodides, carbonyls, bromides
Reaction with hydroxyl radicals	Alkenes, aromatics, hydrogen-containing amines, hydrogen-containing ethers, carbonyls
Physical removal	Ketones, alcohols, esters
Reaction with tropospheric ozone	Alkenes

Risk assessment based toxicity tests and limits were identified, and understanding of situational toxicological constraints underwent considerable evolution. Some chemical options considered for halon replacement (e.g., the perfluorocarbons) were at first embraced, but later discarded as understanding of global warming impact issues developed.

By the time NGP research began in 1997, these efforts had resulted in the birth of new fire extinguishment technologies, a broader view of the chemical options available, and emerging understanding of the dynamics of fire suppression under the adverse conditions encountered during the suppression of in-flight fires in aircraft. The following is a brief summary of these activities and their outcomes.

7.1.2 Fire Suppressant Research - 1974 Through 1993

Scientists at the Naval Research Laboratory had begun investigation of the principles of fire suppression by halon 1301 as early as 1974. This was driven by the Naval Air System Command's desire for a more efficient agent for suppressing in-flight fires. The outcome of this and the few contemporary efforts are summarized in Reference 1. As Rowland and Molina's finding that such compounds could deplete stratospheric ozone became well-known, this research broadened to a variety of fire suppression related topics and potential chemical agents.[2,3] Research at NRL also studied CF_3I flame extinguishment[4,5] and conducted studies of hydrogen fluoride (HF) byproduct formation resulting from halon 1301 fire extinguishment.[6,7]

Beginning in the mid-1980s, the U.S. Air Force (USAF) sponsored research at the New Mexico Engineering Research Institute (NMERI) on “first generation” halon replacement candidates focused on chemicals that were or soon would be readily available and that had a significant amount of known toxicological information.[8] This strategy was adopted for two reasons:

1. Available chemicals could be tested at relatively low cost to determine effectiveness in firefighting scenarios, and
2. Toxicological testing of candidates was expensive and time consuming.

Chemicals developed primarily as chlorofluorocarbon (CFC) replacements were the major focus as first-generation replacements. Relatively large quantities of these chemicals were available, and manufacturers were supporting toxicological testing, as these chemicals were often being considered for applications as refrigerants, solvents, and foam blowing agents, in addition to fire suppression. This strategy proved successful in that a number of halon replacement candidates were identified that were readily available for testing that had a significant amount of toxicity testing already performed.[9,10,11,12,13] Evolving understanding of likely global warming and ozone depletion restrictions as well as the desire for greater agent effectiveness in fire suppression led to a de-emphasis on “first generation” chemicals.

The first generation agents were all halocarbons: hydrochlorofluorocarbons (HCFCs), perfluorocarbons (FCs or PFCs), and hydrofluorocarbons (HFCs). Hydrobromofluorocarbons (HBFC) were also evaluated very early in the program, but were dropped when it became apparent that they would be regulated due to their still significant Ozone Depletion Potentials (ODP). Although the first generation program was successful in identifying available candidates that did not require toxicological testing, the first generation halocarbons were not as effective as the in-use halons and required approximately two to four times more agent. Moreover, some had toxicological and environmental drawbacks. In particular, environmental concerns led to the following restrictions:

- HCFCs would eventually be phased out of production due to their non-zero ODP, and some restrictions are already in place in parts of Europe (and to a limited extent in the USA). The European Community (EC) regulation 3093/94, which entered into force on 1 June 1995, does not allow the use of HCFCs for fire protection.

- Under the Significant New Alternatives Policy (SNAP), the U.S. Environmental Protection Agency (EPA) has applied narrowed limits to the use of perfluorocarbons. PFCs are fully fluorinated compounds, unlike HCFCs or HFCs, and have several attractive features. They are nonflammable, have low toxicity, and do not contribute to stratospheric ozone depletion. The environmental characteristics of concern, however, are their high Global Warming Potentials (GWPs), which are as much as 12,500 times that of carbon dioxide (for a 100 year time horizon), and their long atmospheric lifetimes of up to 50,000 years for CF_4.[14] Although the actual contributions to global warming depend upon the quantities emitted, the long lifetimes make the warming effects of PFCs irreversible. The EPA is allowing the use of PFCs for only selected applications where no other substitute would meet performance or safety requirements.
- HFCs have been prominent as replacements for ozone depleting substances. Nevertheless, they are receiving increasing attention from environmental organizations. The National Institute of Public Health and Environmental Protection, The Netherlands, has projected a significant increase in greenhouse gas emissions due to the use of HFCs to replace CFCs and HCFCs.[15] Moreover, in 1996 Denmark announced that they planed to phase out all hydrofluorocarbons (HFCs) within the next 10 years due to their contributions to global warming.[16]

Early NMERI research on streaming agent replacements for halon 1211 led to the development of methods of estimating atmospheric lifetime and ozone depletion,[17] laboratory scale test methods,[18] methods for evaluation of materials compatibility and operational validation,[19] and preliminary lists of advanced agents (chemically active suppressants).[20]

In 1989, a number of companies involved in the manufacture, sale, and installation of fire suppressant chemicals formed the Halon Alternatives Research Consortium (HARC, which would evolve into the Halon Alternatives Research Corporation). This group's Technical Committee formulated a research plan that would lead to the identification of alternatives to halon 1301 and halon 1211. The first (and only) projects were sponsored by the USAF at the National Institute of Standards and Technology (NIST). The output was two reports:

1. *Preliminary Screening Procedures and Criteria for Replacements for Halons 1211 and 1301*, which was discussed in Chapter 6 of this book.
2. *Construction of an Exploratory List of Chemicals to Initiate the Search for Halon Alternatives*.[21] This report is the first systematic survey since the late 1940s of chemical families and their potentials as halon replacements. Table 7–2 presents the chemical family recommendations resulting from this analysis.

Guiding attributes required of a replacement for halon 1301 included: fire suppression effectiveness, low residue level, low electrical conductivity, low metals corrosion, high materials compatibility, stability under long term storage, low toxicity (inhalation and contact) of the chemical and its combustion products, and low (or zero) contributions to stratospheric ozone depletion and global warming. The report summarized the various mechanisms of flame extinguishment and listed approaches to altering a chemical to decrease its contribution to ozone depletion, including enhancement of chemical reactivity with atmospheric •OH radicals. Finally, the report listed 103 compounds of immediate interest for further testing in flame extinguishment and explosion suppression. Several of the chemical families identified as well as approaches to selecting environmentally acceptable short atmospheric lifetime compounds identified were successfully employed in later studies.

Table 7–2. NIST List of Recommended Chemical Families (1990).

Chemical Family Recommendation	Justification for Further Consideration - Environmental Advantage and Flame Suppression Estimates
Halogenated ketones, anhydrides, esters	Carbonyl absorption max. red shift contributes to photolysis
Unsaturated halocarbons	Reactivity of alkenes to atmospheric •OH radicals
Halogenated ethers and related compounds	Absorption red shift due to C-O-C linkage aides in photolysis
Halons containing iodine	Iodinated halogenated compounds more photochemically reactive and a higher fire suppression efficiency
Sulfur halides	Desirable attributes - Low toxicity, possible significant fire suppression properties
Phosphorus containing compounds	Established fire suppression properties (expected free radical trap mechanism) needs a more volatile or gaseous compound
Silicon and germanium compounds	Silicon in particular (possibly germanium) expected flame suppression effectiveness and short atmospheric lifetime
Metallic compounds	Established flame suppression properties, likely alternative compounds of great interest
Inert gases	Physical suppressant options

The Halon Options Technical Working Conference held its first annual meeting in the spring of 1991. The conference became the premier forum for presentation of research related to halon replacements and, as such, routinely covered topics ranging from new agents and fire suppression equipment to atmospheric science and chemical and suppression by-product toxicology. The compiled papers are available on CD from NIST[22] and at the HOTWC web site, www.bfrl.nist.gov/866/HOTWC.

As early as the first HOTWC, research papers were presented describing the synthesis of compounds which to the present are topics of intense interest. For example, a 1991 paper presented by Dr. J. Adcock of the University of Tennessee detailed his synthesis, under funding by the Electric Power Research Institute, of the low molecular weight brominated fluoroethers that remain of intense interest today.[23] Papers presented by EPA staff covering toxicology and regulatory and toxicological issues provided guidance to the fire research community and those involved in the search for new chemicals. Researchers from private industry presented numerous papers detailing the results of their halon replacement efforts. Many papers detailing agent and equipment development and testing as well as basic extinguishment science were presented by researchers from the military services in the U.S. and overseas.

7.1.3 DoD Technology Development Plan (1993 to 1997)

The Technology Development Plan (TDP) was initiated to identify feasible, commercially available alternatives to ozone depleting substances or use in existing weapons systems.[24] The work was divided among seven Technical Plans. Those involving fire fighting were:

- Technical Plan I. Alternative chemicals, processes and/or techniques for extinguishment of slow growth fires in manned spaces of ships and critical command and control facilities. The best chemical for retrofit was identified as HFC-227ea (C_3HF_7). Fine water mist was noted as a candidate for future platforms.
- Technical Plan II. Alternative chemicals, processes, and/or techniques for extinguishment of slow growth fires in engine nacelles and dry bays of fixed wing aircraft and helicopters. HFC-125 (C_2HF_5) was identified as the optimal chemical for engine nacelle fires. Solid

propellant gas generator technology was promoted for dry bay applications. Perfluorohexane was identified as a streaming agent to replace halon 1211.

- Technical Plan III. Alternative chemicals, processes, and/or techniques for extinguishment of fast growth fires and explosion suppression in unmanned spaces of fixed wing aircraft engine nacelles and dry bays of fixed wing aircraft and helicopters. Completion of this work was deferred.
- Technical Plan IV. Alternative chemicals, processes, and/or techniques for explosion suppression in crew occupied compartments of ground armored vehicles.

All but one of these compounds was less efficient than the halon it would replace, requiring more mass and higher storage volume to achieve comparable performance. Trifluoromethyl iodide (CF_3I) was found to be as effective as the existing halons. However, cardiac sensitization at levels well below the extinguishing concentration restricted further consideration.

There was, therefore, an increasing incentive to look at compounds other than the usual, saturated halocarbons. These compounds are the non-halocarbon candidates, known as "advanced agents." The most promising of these were the phosphorus compounds (particularly, the phosphorus nitrides (which include phosphazenes and phosphonitriles), metal compounds, and silicon compounds. In addition, the broad family of tropodegradable bromocarbons included promising candidates.

7.1.4 Advanced Agent Working Group (AAWG)

On August 23, 1994 representatives of the North Slope Oil Producing and Transmission Companies met with members of the "CF_3I Working Group." The AAWG was formed in the course of this meeting with participating representatives of most of the U.S. military services, NIST, EPA, several fire suppression industry representatives, private consultants, and NMERI. The AAWG funded some of the initial efforts to determine the probability of identifying clean advanced agents for use in normally occupied areas. The work was largely performed at NMERI. Questions posed included:

- What chemically active agent mechanisms were available for protection against fire and explosion?
- What chemical families could provide a replacement for halon 1301 (including preliminary assessments of manufacturability, global environmental impact, and toxicity for these families)?
- What were the prospects for a halon 1301 replacement without major hardware changes?

A listing of specific chemicals was developed for study (Table 7–3). The compounds listed emphasized estimated short atmospheric lifetime and the presence of bromine in the chemical structure. Additional efforts to estimate toxicity, physical properties and more accurately determine fire extinguishment performance through selective testing of some of the compounds listed were initiated.

NMERI assembled physical and toxicological information on the compounds and identified sources and in some cases synthetic methods for these compounds. Toxicological and physical property reviews of this data related toxicity modeling data were performed. Little cardiac sensitization data could be identified at that point and models in existence did not address this particular toxicological end point.

Table 7–3. AAWG Preliminary List of Compounds.

Chemical Formula	Chemical Name	CAS No./Availability
Alkenes		
CH_2=$CHCF_2Br$	3-bromo-3,3-difluoropropene	420-90-6/Commercial sources
CF_2BrCH=$CHCF_3$	*cis*- and *trans*-1-bromo-1,1,4,4,4-pentafluoro-2-butene	
CF_2BrCF_2CH=CH_2	4-bromo-3,3,4,4-tetrafluorobutene	18599-22-9/Commercial sources
$CF_2BrC(CF_3)$=CH_2	3-bromo-3,3-difluoro-2-(trifluoromethyl)propene	
Alcohols		
CF_2BrCH_2OH	2-bromo-2,2-difluoroethanol	420-94-0
$CF_3CFBrCH_2OH$	2-bromo-2,3,3,3-tetrafluoropropanol	94083-41-7
$CF_2BrCF_2CH_2OH$	3-bromo-2,2,3,3-tetrafluoropropanol	
$CF_3CHOHCH_2Br$	3-bromo-1,1,1-trifluoro-2-propanol	Research chemical only
Ethers		
CF_2H-O-CFHBr	(bromofluoromethyl)(difluoromethyl)ether	no CAS Number
CF_2Br-O-CH_3	(bromodifluoromethyl)(methyl)ether	
CF_2BrCH_2-O-CF_3	(2-bromo-2,2-difluoroethyl)(trifluoromethyl)ether	
CF_2BrCF_2-O-CH_3	(2-bromo-1,1,2,2-tetrafluoroethyl)(methyl)ether	13749-39-8
-$CH_2CF_2CBrFCH_2$-O-	3-bromo-2,2,3-trifluorooxolane	
Amines		
$(CBrF_2)(CHF_2)_2N$	bis(difluoromethyl)(bromodifluoromethyl)amine	no CAS Number
$(CBrF_2)(CF_3)(CH_3)N$	(bromodifluoromethyl)(trifluoromethyl)(methyl) amine	no CAS Number
$(CF_3)_2(CH_2CBrF_2)N$	bis(trifluoromethyl)(2-bromo-2,2-difluoroethyl)amine	
$(CBrF_2)(CF_3)_2N$	bis(trifluoromethyl)(bromodifluoromethyl)amine	
Carbonyl Compounds		
$CBrF_2CH_2C(O)H$	3-bromo-3,3-difluoropropanal	
$CH_3C(O)CH_2CF_2Br$	4-bromo-4,4-difluoro-2-butanone	
$CBrF_2CH_2C(O)OCH_3$	methyl 3-bromo-3,3-difluoropropionate	99953-33-0
$CBrF_2CH_2C(O)OCF_3$	trifluoromethyl 3-bromo-3,3-difluoropropionate	
Aromatics		
C_6F_5Br	bromopentafluorobenzene	344-04-7/Commercial sources
$C_6F_5CBrF_2$	(bromodifluoromethyl)pentafluorobenzene	35523-39-8
$C_6BrF_4CF_3$	bromoheptafluorotoluene 2-bromoheptafluorotoluene 3-bromoheptafluorotoluene 4-bromoheptafluorotoluene	113601-46-0 66820-64-2 5360-80-5 17823-46-0

A toxicological quantitative structure-activity relationship (QSAR) relies on the establishment of a statistically significant mathematical correlation between chemical toxicity and a particular chemical, structural, or physical property of a group of similar compounds in order to be used to predict the toxicity of untested chemicals. Further, the predictive accuracy of values and trends is greatest for only for compounds in the same group or very similar groups. QSAR models also included proprietary models for halon property estimation which attempted the estimation of cardiac sensitization LOAEL values.[25]

QSAR modeling of 25 brominated compounds was performed by the U.S. Army Center for Health Promotion and Preventative Medicine (CHPPM) and the British Ministry of Defence (MOD) DERA. U.S. Army CHPPM employed TOPKAT to model QSAR toxicity predictions of acute LD_{50}, LC_{50}, eye sensitization and chronic LOAEL, mutagenicity, DPT, and carcinogenicity.[26] The results of this study are presented in Table 7–4.

Table 7–4. TOPKAT Toxicity Predictions.

Chemical Formula	Acute Toxicity[a]			Chronic Toxicity[a]			
	LD_{50}	LC_{50}	Eye	LOAEL	Mut.	DTP	Carc.
Alkenes							
CH_2=$CHCF_2Br$	o		o	o	X	o	(X)
CF_2BrCH=$CHCF_3$	o	o	X	o	o	o	X
CF_2BrCF_2CH=CH_2	o	o	o	o	o	o	X
$CF_2BrC(CF_3)$=CH_2		o	X	o	X	o	(X)
Alcohols							
CF_2BrCH_2OH	o	o	o	o	o	X	(X)
$CF_3CFBrCH_2OH$	o	o	o	o	o	X	X
$CF_2BrCF_2CH_2OH$	o	o	o	o	o	X	X
$CF_3CHOHCH_2Br$	o	X		X	X		(X)
Ethers							
CF_2H-O-$CFHBr$				X	o		X
CF_2Br-O-CH_3				o	o	o	X
CF_2BrCH_2-O-CF_3				o		o	X
CF_2BrCF_2-O-CH_3	o	o		o	o		X
-$CH_2CF_2CBrFCH_2$-O-				X	X	o	X
Amines							
$(CBrF_2)(CHF_2)_2N$				o			o
$(CBrF_2)(CF_3)(CH_3)N$	o			o			(X)
$(CF_3)_2(CH_2CBrF_2)N$				o	o		X
$(CBrF_2)(CF_3)_2N$				o			X
Carbonyls							
$CBrF_2CH_2C(O)H$	o			o			
$CH_3C(O)CH_2CF_2Br$	o	X	o	o		X	
$CBrF_2CH_2C(O)OCH_3$	o	o		o			(X)
$CBrF_2CH_2C(O)OCF_3$		o		o			(X)
Aromatics							
C_6F_5Br		X	o	X			o
$C_6F_5CBrF_2$		o	X				o
$C_6BrF_4CF_3$		X*	X				o

o	meaningful estimates	X	possibly unacceptable toxicity levels
*	moderate confidence	( )	mixed results on different models
Eye	eye irritation	Carc	carcinogenicity
Mut	mutagenicity		

DERA employed DEREK (Deductive Estimation of Risk from Existing Knowledge), version 15.1,[27] to evaluate the same list of compounds. DEREK is a rule-based software system designed for qualitative prediction of potential toxicity hazards by a chemical based on known structure-activity relationships.

The program does not estimate cardiac sensitization.[28] Four endpoints were evaluated by DEREK, as shown in Table 7–5: carcinogenicity, mutagenicity, sensitization (presumably respiratory) and skin sensitization. In addition, the "rules" incorporated into model skin sensitization (where the program has a tendency to predict false positives) as well as respiratory sensitization, irritation and corrosivity. Acute toxicity is of the highest concern for halon alternatives, but unfortunately is not addressed by the program.

These estimation methods are both highly dependent on the existence of a "training set" of data for similar chemical structures and chemical functional groups in order to establish the correlations and weightings needed to be predictive. Such information is limited, rendering this approach of little use.

Table 7–5. DEREK Toxicity Predictions.

Chemical Family	Chemical Formula	DEREK Prediction
Alkenes	CH_2=$CHCF_2Br$	Skin irritation
	CF_2BrCH=$CHCF_3$	Skin irritation
	CF_2BrCF_2CH=CH_2	Skin irritation, mutagenicity
	$CF_2BrC(CF_3)$=CH_2	Skin irritation
Alcohols	CF_2BrCH_2OH	Skin irritation
	$CF_3CFBrCH_2OH$	Skin irritation, mutagenicity
	$CF_2BrCF_2CH_2OH$	Skin irritation, mutagenicity
	$CF_3CHOHCH_2Br$	Skin irritation, mutagenicity
Ethers	CF_2H-O-CFHBr	Skin irritation
	CF_2Br-O-CH_3	Skin irritation
	CF_2BrCH_2-O-CF_3	Skin irritation
	CF_2BrCF_2-O-CH_3	Skin irritation
	-$CH_2CF_2CBrFCH_2$-O-	Skin irritation, mutagenicity
Amines	$(CBrF_2)(CHF_2)_2N$	Skin irritation
	$(CBrF_2)(CF_3)(CH_3)N$	Skin irritation
	$(CF_3)_2(CH_2CBrF_2)N$	Skin irritation, mutagenicity
	$(CBrF_2)(CF_3)_2N$	Skin irritation
Ethers	$CBrF_2CH_2C(O)H$	Skin irritation, mutagenicity
	$CH_3C(O)CH_2CF_2Br$	Skin irritation
	$CBrF_2CH_2C(O)OCH_3$	Skin irritation
	$CBrF_2CH_2C(O)OCF_3$	Skin irritation
Aromatics	C_6F_5Br	None
	$C_6F_5CBrF_2$	Skin irritation, skin sensitization
	$C_6BrF_4CF_3$ (ortho, meta, para isomers)	None

As an alternative approach, Tapscott and Mather identified some general toxicity trends for alkanes, based on non-quantitative structure activity relationships (SARs) and published toxicity information, from comprehensive reviews of toxicity literature.[29] The identified trends are shown below in rows, with the compound formula followed by $\ln(LC_{50})$ values in mice for 30 min exposures. General trends relating the number of fluorine or hydrogen atoms needed to impart favorable toxicity were not identified. This study indicated that location of substituents appeared to play a more important role than the number of fluorine or hydrogen atoms.

- Toxicity increases in the order F < Cl < Br, for example:

CHF_2CH_2Cl, 2.00	CHF_2CH_2Br, 1.52	$CF_3CHBrCl$, 0.18
CF_3CHFCl, 3.8	CF_3CHCl_2, 2.00	

- For haloethanes, H adjacent to a $-CF_3$ group increases toxicity, therefore, CF_2XCHFX is preferred over CF_3CHX_2 (the X's can be identical or dissimilar halogens and follow the same trend as outlined above). For example:

$CF_2ClCHFCl$, 2.20	CF_3CHCl_2, 2.00	$CF_3CHBrCl$, 1.10
$CF_2BrCHFBr$, 0.45	CF_3CHBr_2, 0.18	
$CF_2ClCHFBr$, 1.42	$CF_2BrCHFCl$, 1.22	

- For halopropanes, the $-CH_3$ group reduces toxicity (at least when opposite a $-CF_3$ group); therefore, CF_3CXRCH_3 is preferred over CF_3CRHCH_2X, where R can be either a halogen or H. For example:

$CF_3CCl_2CH_3$, 2.30	$CF_3CH_2CHCl_2$, 0.88	$CF_3CHClCH_2Cl$, 0.79
$CF_3CHBrCH_3$, 2.03	$CF_3CH_2CH_2Br$, 1.50	

- For halopropanes, $-CH_2-$ groups are favored over $-CF_2-$ groups, for example:

$CHF_2CH_2CClF_2$, 3.00	$CHF_2CF_2CH_2Cl$, 1.62
$CF_2ClCH_2CH_3$, 2.77	$CH_2ClCF_2CH_3$, 2.13

To decrease the toxicity, it is essential that carbon atoms alpha to the carbonyl group contain no halogen atoms. Carbonyl compounds exhibit a range of toxicities depending on whether the carbonyl group is in an aldehyde, ketone, carboxylic acid, or ester.

Toxicity Studies of Tropodegradable Bromofluoroalkenes

Extremely promising inhalation exposure acute toxicity testing at 5 volume %, Table 7–6, of eight bromofluoroalkenes demonstrated no adverse effects in five of the tested compounds.[30] The surprisingly good results from this round of initial testing provided impetus for a greatly expanded program of testing for selected bromofluoroalkenes. The AAWG provided a large part of the funding for this exposure study.

The Ames Mutagenicity test results[31] on the more promising compounds selected based on boiling point were equally reassuring, Table 7−7, as were the results of the chromosomal aberration tests, Table 7−8.[32]

Cardiac sensitization is a property that has been associated with both halogenated and non-halogenated compounds. It has surfaced as a prime consideration in the development of solvents, fire suppressants, and propellants for medical inhalers. It was observed as a cause of cardiac arrest in substance abuse by inhalation of solvents used in spray paints, lubricants, glues and hairsprays, and it has been associated with some pharmaceuticals and volatile surgical anesthesia agents. Known cardiac sensitizing or arrhythmogenic compounds are represented by a wide range of chemical families including alkanes, alkenes, ethers, fluorocarbons, iodocarbons, and bromocarbons.

Table 7–6. Acute Inhalation Toxicity Tropodegradable Bromofluoroalkenes.

Chemical Name	Chemical Formula	Deaths[a] during (post) exposure
1-Bromo-3,3,3-trifluoropropene	$CF_3CH{=}CHBr$	0
2-Bromo-3,3,3-trifluoropropene	$CF_3CBr{=}CH_2$	0
4-Bromo-3,3,4,4-tetrafluorobutene	$CF_2BrCF_2CH{=}CH_2$	0
2-Bromo-3,3,4,4,4-pentafluorobutene	$CF_3CF_2CBr{=}CH_2$	0
2-Bromo-3,3,4,4,5,5,5-heptafluoropentene	$CF_3CF_2CF_2CBr{=}CH_2$	0 (1)
3-Bromo-3,3-difluoropropene	$CH_2{=}CHCBrF_2$	7
2-Bromo-3-trifluoromethoxy-3,4,4,4-tetrafluorobutene	$CH_2{=}CBr(OCF_3)CFCF_3$	10
2-Bromo-3-trifluoromethyl-3,4,4,4-tetrafluorobutene	$CH_2{=}CBrCFC(CF_3)_2$	10

a 10 rats and a 30 min exposure at 5 volume % agent in air

Table 7–7. Ames Mutagenicity Test Results.

Chemical Name	Chemical Formula	Ames Test Result
2-Bromo-3,3,3-trifluoropropene	$CF_3CBr{=}CH_2$	Negative
4-Bromo-3,3,4,4-tetrafluorobutene	$CF_2BrCF_2CH{=}CH_2$	Negative
2-Bromo-3,3,4,4,4-pentafluorobutene	$CF_3CF_2CBr{=}CH_2$	Negative

Table 7–8. Chromosomal Aberration Test Results.

Chemical Name	Chemical Formula	Test Result
2-Bromo-3,3,3-trifluoropropene	$CF_3CBr{=}CH_2$	Negative
4-Bromo-3,3,4,4-tetrafluorobutene	$CF_2BrCF_2CH{=}CH_2$	Negative

The cardiac sensitization test data presented in Table 7–9 represent the only two such tests attempted on bromofluoropropenes.[33,34] While the 1 volume % LOAEL value observed for 2-bromo-3,3,3-trifluoropropene was disappointingly low, making the compound not usable as a halon 1301 replacement, the compound may well be able to serve as a halon 1211 replacement, usable in unoccupied areas. Testing of 1-bromo-3,3,3-trifluoropropene was terminated due to severe adverse effects including tremor.

Table 7–9. Cardiac Sensitization Testing of Bromofluoropropenes.

Chemical Name	Chemical Formula	NOAEL	LOAEL
2-Bromo-3,3,3-trifluoropropene	$CH_2{=}CBrCF_3$	0.5 volume %	1.0 volume %
1-Bromo-3,3,3-trifluoropropene	$CHBr{=}CHCF_3$	a	a

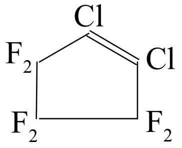
a Determination aborted due to adverse effects on dogs

Further fluorination of these molecules was desirable to reduce boiling points. However, it was unclear where the optimum in degree and pattern of fluorination and site of bromination lay. Given the many additional compounds that had yet to be tested, it was hoped that at least one would have acceptable cardiac sensitization and other toxicity properties to be acceptable for use in occupied areas.

Significant Toxicity Data Source – Inhalation Anesthetic Development

Early compound toxicity efforts were greatly aided by research in anesthesiology, where limited testing results on halogenated alkenes had been reported (Table 7–10).[35] Where provided, the concentrations used were high. The observations in the comments section provided useful compound selection guidance and indicated that study of the related brominated alkenes was worthwhile.

Table 7–10. Anesthesiology Testing of Fluoroalkenes.

Chemical Formula	Animals	Anesthesia	Comments
	2 rats	no	Extreme depression, analgesia, respiratory depression and failure. Death within 18 hours.
$CClF=CClCF_3$	4 dogs	yes	Induction quiet, recovery uneventful, heart slowed with no fall of blood pressure. Brachycardia.
$CF_2=CClCF_3$	1 dog	no	Concentration of 75 %. Marked struggle, gasping, respiratory arrest, revived by artificial respiration.
$CCl_2=CClCF_3$	1 dog	no	Muscular rigidity, pulmonary edema, death after a few hours.
$CHCl=CClCF_3$	2 rats	no	Respiratory depression and failure, one rat died, the other recovered quickly.
$CCl_2=CClCF_3$	3 rats	[a]no/yes	Depression, pulmonary edema, eye irritation, convulsions and death within 1 hour.
$CF_2=CFCF_3$	2 dogs	no	Concentrations of 50 % and 75 %. No demonstrable effect. Tremors, respiratory irritation.
$CH_2=CHCF_3$	2 dogs	no	Tremors, lack of coordination.

a Anesthesia observed for one rat at a higher concentration.

2-Bromo-3,3,3-trifluoropropene, $CH_2=CBrCF_3$, was reported to be an excellent anesthetic with a rapid, uneventful recovery.[36] As the concentrations used were unknown, it was difficult to determine the potency of this chemical as an anesthetic; however, that no adverse effects were observed indicated that this material may have a low toxicity. Studies of 3-chloro-3,3-difluoropropene, $CF_2ClCH=CH_2$, as an anesthetic in dogs showed cardiac arrhythmia with ventricular extra systole, blood pressure decrease, and tremor. Interestingly, inhalation studies later demonstrated that the brominated analogue, $CF_2BrCH=CH_2$, was quickly lethal to rats at an air concentration of 5 volume %.[30]

Overall, the reported live animal toxicity testing performed in the course of anesthesia research provided useful guidance in evaluation candidate compound acute inhalation toxicities and aided early efforts to down-select and target compounds for further synthesis and testing. Efforts to identify suitable anesthesia agents confronted challenges similar to those of interest to the halon replacement community. Suitable anesthesia agents for inhalation needed to be non-flammable and also have low acute toxicity. Low acute toxicity attributes would preferably have included little tendency to induce cardiac arrhythmia.

7.1.5 Summary: Alternative Agents and Selection Criteria Prior to the NGP

The status of alternative agents and development of selection criteria prior to the start of NGP research efforts was dominated by non-brominated fluorocarbons and dry powder extinguishants. In addition, blends of HFCs and HCFCs, combinations of dry powders and fluorocarbons including jelled, agents were in various stages of either commercialization or SNAP approvals. The use of brominated compounds with short atmospheric lifetimes was under consideration for use in streaming applications and as replacements for halon 1301 in massive fire suppression applications such as protection of petroleum production facilities. An almost universal goal of all researchers was the demand by the halon user community for a drop-in replacement agent.

The history of halon replacement development through the mid 1990s reflected concurrent progress in fire technology and basic environmental and atmospheric research areas. In a very real way, halon alternatives development in this era has the appearance of a sequential process of research-based discovery, environmental selection criteria revision followed by rejection of developed alternatives, and a resumption of applied research.

The non-brominated and non-iodinated compounds under consideration were often in commercial use for other purposes. They all suffered from various shortcomings. While they were not ozone depleters because they did not have bromine or iodine in their structures, they did not have short atmospheric lifetimes, and in some cases had significant global warming potentials. Other common weaknesses included significantly higher boiling points, higher toxicity, and high flame extinguishment concentrations. The functional fire suppression related shortcomings were generally highlighted through comparison to halon 1301.

The development of CF_3I reached a critical point prior to the start of the NGP with the announced results of cardiac sensitization LOAEL performance far lower than that of even halon 1211. Use of CF_3I was questioned, and limited risk assessments were performed. The applicability of the test involving epinephrine-challenged dogs was challenged, and the resulting discussion continues. Further, the lack of a useable screening method for cardiac sensitization represented a major financial barrier to the candidate chemical selection process.

Toward the end of the pre-NGP period, the concept arose of incorporating bromine in short atmospheric lifetime (tropodegradable) compounds as a means of achieving more aggressive flame suppression and hopefully reducing agent weight requirements. This desire lead to preliminary lists of potentially tropodegradable compounds. These incorporated molecular features susceptible to attack by atmospheric •OH or •H radicals or tropospheric ozone, photolysis by solar radiation, hydrolysis by atmospheric moisture, or sufficient polarity to dissolve in rain water. Retaining fluorine in the molecule in order to achieve non-flammability and to an extent to reduce boiling point was deemed essential.

7.2 THE NGP APPROACH TO NEW CHEMICALS SCREENING

The NGP search for alternative fire suppressants and, in particular, replacements for halon 1301, was broad in scope, covering nominally the world of chemistry. To ensure that the most optimal chemicals were identified efficiently, a comprehensive search and assessment of a broad array of chemical families and elements was performed.

The 1997 statement of objectives of the nine-year NGP effort was to develop and demonstrate, by 2005, replacements for halon 1301 that were, retrofitable, economically feasible, environmentally acceptable and user-safe processes and techniques and fluids that meet the operational requirements currently satisfied by halon 1301systems in aircraft, ships, land combat vehicles, and critical mission support facilities. The results were to be specifically applicable to fielded weapons systems. By FY2000 this comprehensive goal was restructured and focused on aircraft alone. This change in targeted systems refocused chemical selection efforts on chemical families with the capability to address fire suppression needs in the extreme low temperature conditions experienced by in-flight aircraft. As part of this refocused effort, NGP evaluations of agent low temperature dispersion, aircraft fire incidence and fire risk assessment were conducted. These studies are detailed in Chapters 2 and 8, and they significantly reduced the sole chemical selection boiling point criterion at a midway point in the Program.

As noted in Chapter 6, these surveys typically began with an assessment of available literature information on physical properties, toxicity, and flame suppression. A second step involved estimation of these properties, where possible. Promising chemical families were subject to increased scrutiny, and in some cases representative compounds were obtained and flame suppression tests run. Where unusually interesting, and especially previously unexamined, chemical families were identified, limited mechanistic studies were performed and often individual projects were largely dedicated to their study.

The criteria for further serious consideration of a compound as a candidate for suppression for in-flight aircraft fires were delineated in Chapter 6:

- Cup burner flame extinguishment level measured or estimated to be below 5 volume %. To better this 5 volume % limit, a compound had to catalytically suppress combustion or have a high heat capacity.
- Boiling points below about 20 °C. For fluids with slightly higher boiling points, similar fluids were considered to see if there might be a lower boiling member of the chemical family.
- Inclusion of a chemical feature that rendered the chemical tropodegradable, i.e., likely to have a short atmospheric lifetime.
- Absence of any toxicological data showing that serious effects on people could occur at a concentration lower than that needed to effect flame extinguishment.

As the early NGP research progressed, some chemical families were found unsuitable, while others of promise were identified.[37,38] About one-third of the way into the Program, the NGP performed a detailed analysis of the state of knowledge of the chemical families.[39] The goal of this review was to identify chemical families still in need of scrutiny as potential flame suppressants and halon replacements, to list those chemical families for which sufficient knowledge existed to select the best candidates, and to identify those families unlikely to contain useable alternative fire suppressing chemicals. Allowance for otherwise desirable candidates with somewhat elevated boiling points was made. The available data for each family was reviewed and a consensus reached on chemicals for further investigation and those for which further study was not warranted. Priorities were divided into three groups, as shown in Table 7–11:

- High Priority: Families that had not been extensively studied and for which there was high promise to yield one or more candidates.
- Further Study: Families for which limited data indicated promise to yield one or more candidates.
- Quick Look: Families that were relatively unstudied and whose potential was unclear or for which the cost of the compounds might prohibit a full study.

Table 7–12 lists the wide range of chemical families for which further study was not recommended and the primary reasons for those decisions.

Table 7–11. Chemical Families Selected for Further Study.

Chemical Family	Recommendation		
	High Priority	Further Study	Quick Look
Iodine containing alkanes and alkenes		X	
Bromine containing alkenes	X		
Iodine containing ethers			X
Bromine containing ethers		X	
Bromine containing alcohols			X
Fluorine containing aldehydes and ketones		X	
Nitriles			X
Fluoro- and bromofluoroamines	X		
Sulfoxides			X
Phosphorus containing Acids and Esters			X
Phosphonitriles and Phosphorus halides		X	
Copper containing Compounds			X
Manganese containing Compounds	X		
Iron containing compounds		X	
Tin containing compounds	X		

Table 7–12. Chemical Families Not Pursued Further.

Chemical Family	Major Disqualifying Finding		
	Well Studied	Toxicity, Colligative Property or Other Drawback	Suppression Efficiency or Flammability
Brominated, chlorinated and fluorinated alkanes	X		
Chlorinated alkenes		X	X
Fluorinated alkenes			X
Alkynes			X
Iodinated ethers		X	
Chlorinated ethers			X
Fluorinated ethers	X		
Iodinated or chlorinated alcohols		X	
Fluorinated alcohols		X	X
Iodinated or brominated aldehydes & ketones		X	
Chlorinated aldehydes & ketones		X	X
Halogenated (I, Br, F) aromatics		X	
Nitro compounds		X	X
Nitrates, nitrites, nitroso compounds		X	
Hexavalent sulfur		X	X
Difluorosulfur compounds		X	
Phosphines or pentacoordinate Phosphorus		X	
Alkali metal or alkaline earth compounds	X		
Boron and aluminum compounds			X
Titanium, antimony, germanium or silicon - containing compounds		X	

A summary of the several broad survey efforts to identify chemical families with the potential to yield suitable effective and environmentally acceptable halon replacements is presented in the following sections. The material presented describes selection approaches, chemical family evaluations, and the limited testing done to confirm extinguishment performance.

Separate presentations of the focused studies of fluoroalkyl phosphorus compounds and low boiling tropodegradable chemical families of flame suppression performance are located in Section 7.4. A limited presentation of work on phosphorus halide extinguishants such as PBr_3 is discussed later in Section 7.3.5. A broad discussion of phosphorus and metal fire extinguishment chemistry is presented in Chapter 3 of this book.

7.3 NGP SURVEYS OF INORGANIC CHEMICAL FAMILIES

7.3.1 Main Group Elements - Group I

The term "main group elements" is used to denote any elements other than transition metals. Figure 7–1 represents a periodic table with the elements being considered in boldface. Note that carbon, oxygen, and the halogens may be (in some cases, are likely to be) present; however, such elements do not form the primary structural features of the compounds considered here. As noted earlier, some nitrogen compounds were examined in earlier work; others are discussed in section 7.4. Helium, neon, and argon were considered in their elemental form. Due to their toxicity, the radioactive elements were excluded. Though they were included, the Group I and Group II elements were unlikely to have utility as defined here since most compounds of these are solids.

Group I elements comprise the alkali metals: lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr). The last element is radioactive and was not considered. Compounds of the alkali metals, in particular potassium and sodium salts, have long been used as fire extinguishing agents. A thorough review of the literature on fire extinguishment by compounds of the Group I elements has been prepared,[40] and these elements have also been discussed in a report prepared for the USAF.[20] These compounds were highly effective extinguishants but the suppression mechanism was uncertain. Extinguishment may be due to heat absorption, free-radical recombination on particulate surfaces, or homogeneous free-radical removal. Heat extraction did not account for the high extinguishment efficiencies of these elements.

I	II		III	IV	V	VI	VII	VIII
								He
Li	**Be**		**B**	C	N	O	F	**Ne**
Na	**Mg**		**Al**	**Si**	**P**	**S**	Cl	**A**
K	**Ca**		**Ga**	**Ge**	**As**	**Se**	Br	**Kr**
Rb	**Sr**	**Transition Metals**	**In**	**Sn**	**Sb**	**Te**	I	**Xe**
Cs	**Ba**		**Tl**	**Pb**	**Bi**	Po	At	Rn
Fr	Ra							

Figure 7–1. Groups and Elements Studied.

Nearly all compounds of the Group I elements are solids at room temperature, and, therefore, past work has been on either dry chemical powders or aqueous solutions. Exceptions are some of the lithium alkyls, which are flammable. Some eutectic mixtures of alkali metal salts have melting points near room temperature; however, the vapor pressures are negligible. Studies have shown that aqueous solutions of some alkali metal compounds are extremely effective fire extinguishants,[41] as are alkali metal powders (Chapter 4). However, these have been rejected for aircraft application due to their corrosion threat. Given the more mature state of knowledge and demonstrated effectiveness of sodium, potassium, and phosphorus based powders, any less efficient powders of other elements did not warrant consideration.

7.3.2 Main Group Elements - Group II

No flame extinguishment data have been found for compounds of beryllium. However, compounds of the other Group II elements (excluding, of course, radium) have been shown to have lower fire extinguishing efficacies than those of the Group I compounds. Since these Group II compounds are also solids, compounds of the Group II elements were not considered further.

7.3.3 Main Group Elements - Group III

Boron

A number of boron compounds are gases or liquids; however, apparently without exception all are either flammable, highly toxic, or act merely as carriers where, as a part of the molecule, they bring halogen atoms into the combustion zone. The known gaseous and liquid boranes (boron hydrides) are flammable. Many of the simple halides, such as BF_3, B_2Cl_6, etc., are highly unstable in the presence of moisture and are all highly toxic.

Fire extinguishment testing using standard handheld extinguishers had shown that finely divided borax ($Na_2B_4O_7$, degree of hydration not specified) was approximately equal to sodium bicarbonate in fire extinguishment effectiveness.[42] The fire suppression efficiency of this compound may be due to the presence of sodium.

Common flame retardants for fabrics and plastics are sodium borate pentahydrate (borax pentahydrate, $Na_2B_4O_7 \bullet 5H_2O$), boric acid ($B(OH)_3$, boric oxide (B_2O_3), disodium octaborate tetrahydrate ($Na_2B_8O_{13} \bullet 4H_2O$), ammonium pentaborate octahydrate [$(NH_4)_2B_{10}O_{16} \bullet 8H_2O$], and the zinc borates (e.g., $Zn_4B_{12}O_{22} \bullet 7H_2O$).[43] In an extensive study of boron compounds, sodium tetrafluoroborate ($NaBF_4$), a solid, was the most effective single compound for reducing fabric flammability.[44] These flame retardants are all solids.

In this study, no liquid or gaseous boron compounds were found that have a reasonable toxicity and that are nonflammable. There was also no evidence that boron has any catalytic fire suppression capability.

Aluminum

Aluminum oxide trihydrate ($Al_2O_3 \bullet 3H_2O$) is a widely used fire retardant in elastomers,[45] where it operates primarily by endothermic release of water to provide cooling. Gaseous aluminum chloride had been shown to be an effective inhibitor of premixed methane/air flames,[46] and the dispersed powder effectively inhibited spark ignition of methane/air mixtures.[47] This activity was probably due to the presence of chlorine rather than to the aluminum itself. To date, no evidence that aluminum has any catalytic fire suppression capabilities has been presented. Moreover, the few gaseous or liquid aluminum compounds that exist have serious drawbacks (toxicity, flammability, and/or stability).

Gallium, Indium, and Thallium

No fire extinguishing studies have been reported for these three relatively rare elements. This may be due to the realization that toxicity would present a serious barrier to use of any thallium or indium compounds as extinguishants.

7.3.4 Main Group Elements - Group IV

Carbon

Carbon is the structural core of organic compounds, which are discussed in Section 7.4. There is no reason to expect that solid carbon particles are effective fire suppressants, as they would act as fuel and oxidize to CO and CO_2. It is possible that flame radiation absorption by particulate carbon may aid in suppression, but no evidence exists that carbon imparts any catalytic fire suppression capability.

Silicon

Silicon compounds have been examined in several projects,[37,38,48,49] and there is little evidence that silicon offers any inherent fire suppression capabilities. The presence of silicon may, in some cases, offer desirable environmental (improved rain-out due to hydrolysis to polar species) and toxicological (through chemical decomposition) characteristics or physical properties.

The chemistry of silicon compounds related to compounds of interest in the development of fire suppressants has been reviewed in detail.[49]

Due to the complexity of the syntheses, no attempt was made to prepare fluoroalkyl-containing silicon compounds during the NGP. Table 7–13 lists those silicon compounds selected for testing to obtain at least some baseline data.[49]

Table 7–13. Silicon-containing Compounds.

Chemical Name	Formula	T_b (°C)	Flash Point, °C
Silicon tetrachloride	$SiCl_4$	57.6	None
Bromotrimethylsilane	$SiBr(CH_3)_3$	79	32
Silicon tetrabromide	$SiBr_4$	153	None

Silicon tetrachloride ($SiCl_4$) has a relatively low boiling point; however, this compound caused problems with the Standard NMERI Cup Burner. During the first test, the metering valve on the cup burner apparatus became increasingly difficult to adjust and finally froze. Upon disassembly, the valve and line leading to the valve were found to be clogged with particulate matter. It is likely that silicon dioxide was formed by hydrolysis. No further testing was attempted; however, with care, it is likely that the Modified NMERI Cup Burner could be used for this or similar compounds in the future.

Bromotrimethylsilane ($SiBr(CH_3)_3$) was tested using the Modified NMERI Cup Burner. With a boiling point of 79 °C, this compound was relatively easily volatilized; however, the material is flammable. Two tests gave cup burner extinguishment concentrations of 2.3 volume %. As the flow of the compound was increased, there appeared to be some effect on the flame, although no distinct lifting of the flame off the fuel cup was observed. The flame wandered around, occasionally falling down the side of the cup. When the flow reached 0.043 g/s, the flame behaved erratically and traveled to the bottom of the chimney (to the glass beads). The flame in the fuel cup was extinguished, but the compound continued to burn on the surface of the glass beads. A small amount of the compound was found to sustain a flame.

Silicon tetrabromide ($SiBr_4$), as expected, was more effective than the other silicon compounds tested. The first test with the Modified NMERI Cup Burner gave an extinguishment concentration of 2.0 volume %. During subsequent testing, however, serious problems with clogging of the syringe pump were encountered. Cleaning the syringe completely and repeating the test resulted in the same problem. This cast doubt on the extinguishment value of 2.0 volume % obtained in the first test. If the syringe were sticking, the measured flow would have been less than the actual flow, because the syringe pump was allowed to slip for safety. This would have resulted in a low cup burner value.

Silicon Compound Fire Suppression Mechanism

A past review of the chemistry and fire suppression properties of silicon compounds had been presented in Reference 49. Except as otherwise stated, all of the information presented here was newly acquired or is an expansion of information contained in that source. Of particular interest as fires suppressants were silicon-containing compounds with fluorinated alkyl groups. Fluoro-organosilicon polymers have been of some commercial interest.[50]

Many organosilicon materials are relatively stable, inert, have a low toxicity, and have lower atmospheric lifetimes than do closely related carbon compounds. This allows the incorporation of bromine in silanes and siloxanes without having unacceptably large ODP values. While silicon compounds without bromine do not appear to have significant fire suppression capabilities, the addition of bromine could provide a compound with good fire suppression capability while maintaining good environmental characteristics.

Overall, there was little evidence that silicon itself plays a significant role in flame extinguishment, even though one could propose combustion free radical recombination cycles such as those in Reactions 7-1 and 7-2, similar to those proposed for other metals.[51]

$$\mathrm{SiO\bullet} + \mathrm{\bullet H} + \mathrm{X} \rightarrow \mathrm{SiOH} + \mathrm{X^*} \qquad (7\text{-}1)$$

$$\mathrm{SiOH} + \mathrm{\bullet H} \rightarrow \mathrm{H_2} + \mathrm{SiO\bullet} \qquad (7\text{-}2)$$

The combustion and explosive properties of dichlorosilane (SiH_2Cl_2) have been thoroughly studied.[52] Polyorganosiloxanes and inorganic silicates have been examined as potential flame retardants.[53] The major mode of reaction is the formation of protective surface coatings during a fire. The flammability of silicone polymers has been reduced through addition of fluorine, bromine, and CCl_3 groups.[54]

Claims have been made that liquid fire extinguishing compositions containing haloalkanes and cyclic polysiloxanes increase penetration and throw distance.[55] However, there has been no claim that the silicon-containing compounds actually increase the intrinsic fire suppression capability.

Silicon Compound Atmospheric Lifetime, ODP, and GWP

Silicon, and other metalloids and metals, are known to be deposited in the upper atmosphere by meteors; however, it is believed that only the more polar metal oxides (e.g., sodium oxide) are likely to have any direct homogeneous chemical effect on atmospheric chemistry since these compounds have weak metal-oxygen bonds and can regenerate free atoms through photolysis and reactions with •O and •OH.[56] On the other hand, it must be recognized that silicon-containing particulates could play a significant role in heterogeneous atmospheric chemistry.[57] The silicon-oxygen bond is quite strong compared with the sodium-oxygen bond in the simple diatomics (Si-O, 799.6 kJ/mole; Na-O, 256.1 kJ/mole).[58] Thus, reactions proposed for ozone depletion by sodium (Reactions 7-3 and 7-4) are unlikely for ozone depletion by silicon.[59] Sodium atoms generated in the atmosphere may also enhance ozone depletion by chlorine[60] although it is not known whether similar enhancement by silicon takes place. Note, however, that since approximately 40 metric tons to 300 metric tons of metals are deposited daily by meteorites[61] and since silicon is one of the more abundant elements in meteorites[60] it is unlikely that anthropogenic silicon would produce a significant atmospheric effect in comparison to other sources.

$$\bullet\mathrm{Na} + \mathrm{O_3} \rightarrow \bullet\mathrm{NaO} + \mathrm{O_2} \qquad (7\text{-}3)$$

$$\bullet\mathrm{NaO} + \bullet\mathrm{O} \rightarrow \bullet\mathrm{Na} + \mathrm{O_2} \qquad (7\text{-}4)$$

Rate constants for reactions of some silicon compounds with •OH free radicals and estimated lifetimes based on those rate constants are presented in Table 7–14.

Methane (CH_4) has a rate constant of 0.0836×10^{-12} cm^3/molec-s at 298 K[62], a value considerably smaller than that found for silane (SiH_4). This is, however, undoubtedly due to the lower Si-H bond strength in SiH_4 (bond strengths: H-SiH_3, 384.1 kJ/mole; C-CH_3, 438.9 kJ/mole).[58] Of greater interest are rate constants for silicon-containing molecules with no Si-H bonds. 2,2-Dimethylpropane ($C(CH_3)_4$) has an •OH rate constant of 0.875×10^{-12} cm^3/molec-s at 298 K, which is slightly smaller than that of tetramethylsilane ($Si(CH_3)_4$). Unfortunately, other data allowing a direct comparison between C-H bond rate constants for carbon and silicon compounds were unavailable. Thus, there appeared to be no reason to assume that, in the absence of Si-H bonds, silicon compounds were inherently more reactive toward •OH than are carbon compounds.

Maximum rate constants (no reaction observed) on the order of 10^{-21} cm^3/molec-s have been determined for the reaction of O_3 with silicon-containing compounds.[63] These data gave minimum estimated lifetimes of the order of 2500 days. Thus, there would be little, if any, removal by tropospheric ozone.

In general, silicon compounds are considerably more unstable toward hydrolysis than are carbon compounds, and this property may provide an effective removal route for many of these materials. The Si-halogen bond hydrolyzes readily; however, the rapidity of this hydrolysis (and the resulting formation of toxic products) eliminates the consideration of compounds containing halogens bonded directly to silicon as fire suppressants (other than for basic laboratory studies). Compounds containing Si-H bonds also hydrolyze relatively easily when the pH is greater than 7, but are relatively stable in acidic solution. The alkoxy-Si bond is subject to hydrolysis and cleavage can cause condensation to higher polymers. Note, however, that this is highly dependent on the absence of steric hindrance. Alkoxy-substituted silanes with larger alkoxy groups are much more stable toward hydrolysis.[64] Silanes containing only carbon bonded to silicon are relatively hydrolytically stable.

Table 7–14. •OH Rate Constants for Silicon Compounds.

Chemical Formula	k_{OH}, cm^3/molec-s	Atmospheric Lifetime, days[a]
SiH_4[b]	12.2×10^{-12}	0.97
$Si(CH_3)H_3$[b]	34.3×10^{-12}	0.35
$Si(CH_3)_2H_2$[b]	44.8×10^{-12}	0.27
$Si(CH_3)_3H$[b]	26.7×10^{-12}	0.45
$Si(CH_3)_4$[b]	1.09×10^{-12}	10.9
SiH_4[c]	[d]$12.4 \pm 1.9 \times 10^{-12}$	0.96
$Si(C_2H_5)_4$[c]	[e]75×10^{-12}	0.16
$Si(CH_3)_4$[f]	[d]$1.00 \pm 0.09 \times 10^{-12}$	11.9
$(CH_3)_3SiOSi(CH_3)_3$[f]	[d]$1.38 \pm 0.09 \times 10^{-12}$	8.6
$[(CH_3)_2SiO]_3$[f]	[d]$5.2 \pm 1.1 \times 10^{-13}$	22.9
$[(CH_3)_2SiO]_4$[f]	[d]$1.01 \pm 0.20 \times 10^{-12}$	11.9
$[(CH_3)_2SiO]_5$[f]	[d]$1.55 \pm 0.30 \times 10^{-12}$	7.7
$(CH_3)_3SiOSi(CH_3)_2OH$[f]	[d]$1.89 \pm 0.36 \times 10^{-12}$	6.3

a Lifetimes estimated using globally averaged •OH model.
b Personal communication from Dr. Paul Marshall, Department of Chemistry, University of North Texas, Denton, to Dr. Robert E. Tapscott, 27 May 1997. Values are at 295 K.
c Reference 62
d Value at 297 K
e Value at 793 K
f Reference 63

Silicon compounds are expected to be more susceptible to photolysis than are the corresponding carbon compounds. The laser-induced photodissociation of silanes is one method used for vapor deposition of silicon films in the production of microelectronics.[65]

A few, scattered, and, in some cases suspect, lifetime and GWP data have been reported for silicon-containing compounds.[49] Siloxanes have been reported to have atmospheric lifetimes of from 10 days to 30 days.[66]

It was concluded that silicon compounds are unlikely sources of stratospheric ozone depletion due to the presence of silicon only. When hydrogen atoms are present, limited data indicated effective removal by tropospheric •OH and short atmospheric lifetimes. Insufficient data were available to judge tropospheric removal and atmospheric lifetimes for silicon compounds containing no hydrogen, with one exception. Silicon compounds containing direct Si-halogen bonds hydrolyze rapidly and give short atmospheric lifetimes; however, such compounds were unsuitable for halon substitutes due to their expected high toxicity. Photolysis may be a potential route to atmospheric removal in some cases. Of particular interest was possible photolytic "synergism" when both silicon and bromine were present; however, no data existed to evaluate such "synergism." Unfortunately, there were no atmospheric data for fully halogenated organosilicon compounds containing no Si-H or Si-halogen bonds (and, in particular, compounds containing primarily fluorine as the halogen). Such compounds are unlikely to be removed rapidly by hydrolysis, rainout, or other processes, with the possible exception of photolytic decomposition. In summary, although there was no evidence that silicon compounds will have unacceptable global atmospheric environmental properties (e.g., unacceptable ODP, GWP, or lifetime), this may not be true for fully halogenated silicon compounds containing no Si-H or Si-halogen bonds.

Finally, silicon compounds were expected to have few if any global atmospheric impacts. This may be the case even when bromine is present. There is, however, a real need for studies of the photochemistry of bromine-containing silicon compounds.

Silicon Compounds - Toxicity

Compounds containing silicon bonded to halogens are highly toxic owing to rapid hydrolysis of the silicon-halogen bond, although the inhalation toxicity of $SiCl_4$ is moderate.[67] Limited testing of industrial chemicals indicated that stable silane derivatives have a low toxicity. A number of siloxanes used industrially have a low toxicity.[67]

One paper not presented in Reference 39 reported that no toxic signs were found for four male rats to a single 6-hour exposure at 8000 μL/L or to 15 6-hour exposures at 1000 μL/L for tetramethylsilane, $Si(CH_3)_4$.[68] In the same study, 20 6-hour exposures of four female rats to diphenyldimethoxysilane, $Si(C_6H_5)_2(OCH_3)_2$, at its saturation vapor pressure showed no adverse effects.

A recent EPA final action on significant new uses listed potential toxicity hazards for a number of silicon compounds.[69] The final rule stated that alkoxysilanes can cause lung toxicity and severe irritation to skin, eyes, and mucous membranes. Of particular interest is the finding that "Based on analogy to alkoxysilanes and perfluoro compounds," $Si(OCH_3)_3(CH_2CH_2CF_2CF_2CF_2\text{-}CF_2CF_2CF_2CF_2CF_3)$ may cause lung toxicity, irritation to mucous membranes, liver toxicity, blood toxicity, immunosuppression, and reproductive toxicity. In part, this finding may have been due to the analogy between the fluoroalkyl chain and some HFCs; it may have had little or nothing to do with the silicon atom.

There is only a relatively small amount of toxicity data available for the silicon compounds of primary interest here (compounds containing halogenated alkyl groups and no direct Si-halogen bonds). In general, siloxanes have moderately low toxicities. Alkoxy-containing silicon compounds could cause irritation to skin, eyes, and mucous membranes. The presence of Si-halogen bonds is expected, in all cases, to cause severe toxicity problems due to hydrolysis with formation of hydrohalic acids. Such compounds are probably unacceptable as halon substitutes.

Silicon Compound Chemistry

Silicon chemistry has been the subject of a number of relatively recent reviews (e.g., the papers in Reference 70); however, the number of nonflammable silicon compounds that can be considered for halon replacement is small.

Silicon compounds offer relatively little promise. The silicon itself contributes little to fire suppression effectiveness, and many of the most interesting compounds (e.g., those containing bromofluoroalkyl and/or fluoroalkyl groups) have been difficult to synthesize. Of particular concern was the instability of compounds containing $-CF_3$ groups immediately adjacent to the silicon atom, and such compounds were not considered further. Compounds in which -OR and/or $-OCF_2Br$ groups are attached to the silicon atom have low volatility and high viscosity.

A series of bromoalkylsilanes were prepared in a two-step synthesis from a halomethane and a bis(trimethylsilyl)amide.[71] The preparation is shown in Reactions 7-5 and 7-6, where "M" is sodium or potassium and "R" is a nonfluorinated (compounds containing fluorine on a carbon atom adjacent to silicon are usually unstable) haloalkyl group.

$$(M^+ [(CH_3)_3Si]_2N^-) + RH \rightarrow [(CH_3)_3Si]_2NH + (M^+ R^-) \tag{7-5}$$

$$(M^+ R^-) + (CH_3)_3SiCl \rightarrow (CH_3)_3SiR + MCl \tag{7-6}$$

The reaction of trialkylchlorosilane ($SiClR_3$) with chlorotrifluoroethene ($CClF{=}CF_2$) allowed the synthesis of a number of trifluorovinylsilanes ($CF_2{=}CFSiR_3$).[72] Bromination or hydrobromination of the double bond may permit the formation of the compounds $CBrF_2CBrFSiR_3$, $CBrF_2CHFSiR_3$, and $CHF_2CBrFSiR_3$.

A series of tetra(fluoroalkoxy)silanes ($Si(OR)_4$) have been prepared by reaction of the appropriate fluorinated alcohol with silicon tetrafluoride (SiF_4).[73] All of the compounds are liquids at room temperature, Table 7−15; the melting points are low, (less than -68 °C except for $Si(OCH_2CF_3)_4$). However, the boiling points and viscosities are high. One major problem with such alkoxy compounds is that they hydrolyze readily and then polymerize.

Table 7–15. Tetra(fluoroalkoxy)silanes.

Chemical Name	Formula	T_b °C (kPa)	Liquid density g/mL (°C)	Liquid viscosity, 20 °C (cp)
Tetrakis(2,2,2-trifluoroethoxy)silane	$Si(OCH_2CF_3)_4$	155.5 to 157 (99)	1.5107 (20)	2.2089
Tetrakis(2,2,3,3-tetrafluoropropoxy)silane	$Si(OCH_2CF_2CHF_2)_4$	117 to 118 (0.5)	1.5927 (20)	18.92
Tetrakis(2,2,3,3,4,4,4-heptafluorobutoxy)silane	$Si(OCH_2(CF_2)_2CF_3)_4$	96 to 97 (0.5)	1.5740 (71.1)	7.613
Tetrakis(2,2,3,3,4,4,5,5-octafluoropentoxy)silane	$Si(OCH_2(CF_2)_3CHF_2)_4$	156 to 159 (0.3)	1.8150 (20)	42.75
Tetrakis(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoropentoxy)silane	$Si(OCH_2(CF_2)_5CHF_2)_4$	201 to 204 (0.4)	1.7181 (71.1)	108.8
Tetrakis(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluorononoxy)silane	$Si(OCH_2(CF_2)_7CHF_2)_4$	[a]235 to 240 (0.3)	Not reported	Not reported

a With decomposition.

Overall it was determined that there was insufficient basis for continued consideration of silicone-based compounds as halon replacements.[39]

Germanium, Tin, and Lead

The only germanium compound studied as a fire extinguishant was germanium tetrachloride, $GeCl_4$,[74] whose extinguishing capability was primarily due to the presence of the chlorine atoms. On the other hand, there is evidence of strong chemical inhibition for compounds of tin and lead (Chapter 3). Thus, lead tetra-acetate ($Pb(CH_3COO)_4$) and lead acetylacetonate, $Pb(CH_3C(O)CHC(O)CH_3)_2$), neither of which contain halogens, are effective extinguishants.[75] A catalytic mechanism has been proposed for fire extinguishment by tin.[76] A recent paper presented results indicative of a weak catalytic flame suppression action by tin compounds.[77]

Despite the scattered indications of catalytic effects for compounds of the heavier Group IV elements, germanium is too costly to be considered, and tin and lead are environmentally unacceptable as well as toxic to animals. Heavy metal toxicity is a well recognized and extensively documented environmental concern.

7.3.5 Main Group Elements - Group V

Inorganic Nitrogen

The chemistry and flame suppression of nitrogen compounds (with an emphasis on fluoroalkyl amines) was discussed in earlier work performed under the NGP.[37,38] One cycle that has been proposed to catalyze recombination of hydrogen atoms and hydroxyl free radicals is given in Reactions 7-7 through 7-9.[78] The NO cycle, however, appears to be relatively inefficient.[79]

$$H + NO + M \rightarrow HNO + M^* \tag{7-7}$$

$$H + HNO \rightarrow H_2 + NO \tag{7-8}$$

$$HNO + OH \rightarrow H_2O + NO \tag{7-9}$$

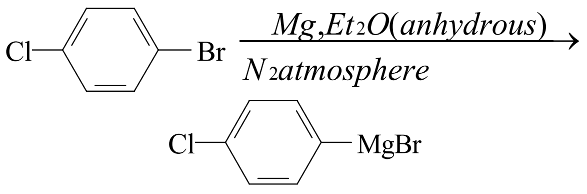
Inorganic Phosphorus

A search of the Chemical Abstracts Database for the key words “flame,” “fire,” and “flammable” coupled with “phosphonitriles” and related terms yielded 366 references, nearly all of which were for fire retardants for polymers. These included reviews of cyclo- and polyphosphazenes as fire retardants and as fire resistant materials.[80,81]

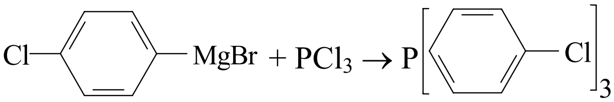
The mechanisms of fire retardancy of solids by phosphorus-containing compounds have been studied for decades.[82] Depending on the specific compound and the host polymer, these additives act in the gas and/or condensed phases.[83] The details of the mechanism are still debated, as evidenced in papers presented at the annual Business Communications Company (BCC) Conference on Flame Retardancy.

Phosphorus and bromine behave as synergistic flame retardants, and the greatest synergism appears to be when the two elements are combined in the same molecule.[84,85] It has been proposed that in polyesters, compounds containing both phosphorus and bromine act in two separate roles as flame retardants.[86] The work cited indicated that the phosphorus induced formation of aromatic residues and char, which reduced the transport of gases to the flame. The bromine was believed to reduce the overall oxidation rate, reducing the heat transported back to the solid.

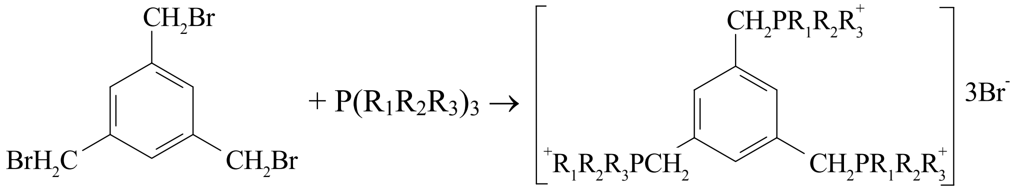
The preparation of halogenated triaryl phosphines as flame retardants has been reported.[87] An example is shown in Reactions 7-10 and 7-11 for tris(parachlorophenyl)phosphine (solid, melting point 106 °C). A number of phosphonium salts have also been prepared, as shown in Reaction 7-12, where R_1, R_2, and R_3 are various alkyl and aryl groups. All of these materials are solids.



(7-10)



(7-11)



(7-12)

Resorcinol bis(diphenyl phosphate) (Figure 7–2, n = 1 to 8), a polymeric material containing no halogen, has been reported to act as a flame retardant additive.[88] The material, which is made from phosphorus oxychloride, resorcinol, and phenol, is a colorless to light yellow liquid with a viscosity of 600 cp at room temperature and 100 cp at 55 °C.

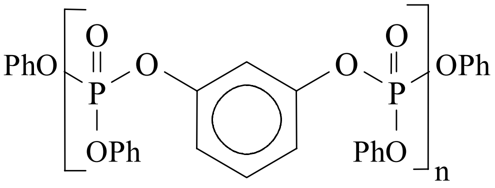


Figure 7–2. Resorcinol.

Phosphorus-containing groups have been incorporated directly onto polymeric molecules rather than using phosphorus additives to provide flame retardancy. Fire resistant organosilicon polymers have been prepared by incorporation of phosphazenes.[89] Resins containing melamine combined with triethylphosphate and dimethylmethylphosphonate have been reported as flame retardants.[90] A number of compounds containing vinyl groups attached to phosphorus have been prepared to permit copolymer formation (e.g., Figure 7–1[91]). It is believed that when incorporated directly into a polymer, these materials provide flame retardancy primarily by char formation.

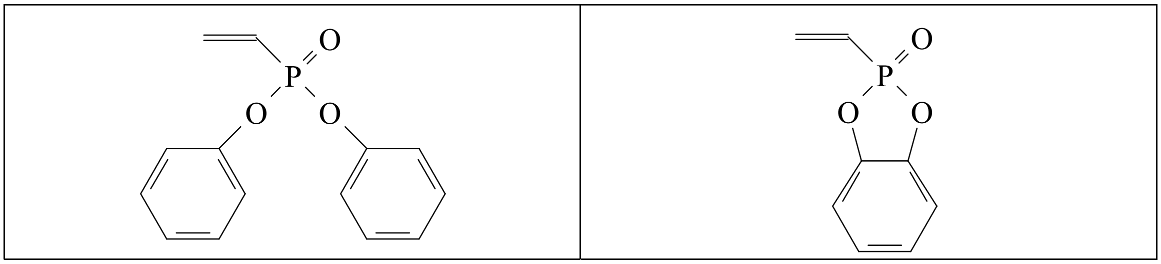


Figure 7–3. Vinyl Phosphonates.

The large variability in toxicity of phosphorus compounds and the possibility of cholinesterase inhibition raised toxicity concerns with these compounds. In general, their toxicity decreases as the oxidation state of the phosphorus increases, i.e., phosphines are generally the most toxic and phosphates are the least toxic. Phosphonitriles appear to have relatively low toxicities, but mutagenicity may be of concern. Compounds with phosphorus-halogen bonds are probably unacceptable as halon substitutes. Phosphorus chemistry has been the subject of a number of relatively recent reviews (e.g., the papers in Reference 92); however, most of this work has been on nonvolatile or flammable chemicals.

Chapter 3 and Reference 93 provide good overviews of phosphorus chemistry as it applies to chemicals of interest as fire suppressants. A review of NGP testing of phosphorus compounds is consolidated in Section 7.4.4.

Phosphonitriles

Among the phosphorus compounds, phosphonitriles have been of primary interest as replacement fire suppressants in the past; however, there are relatively few that have sufficiently high volatility to replace halon 1301. There may, however, be some interest in using these materials in carriers for some applications.

The linear phosphonitriles, for which preparations have been reported,[94] are considerably more reactive than the cyclic compounds, particularly toward hydrolysis.[95] This makes them somewhat less attractive than the cyclic materials for study as halon 1301 replacements. The reactivity of the 3-membered ring system $P_3N_3Cl_6$ toward chloride exchange is lower than that of the four-membered and larger cyclics.[96]

Of particular interest are the fluorinated phosphonitriles. Fluorination normally occurs as geminal substitution; however, procedures for making nongeminal derivatives have been reported.[97] Although a number of chloro- and fluoro-substituted bis(dimethylamino)-cyclotriphosphonitriles have been reported[98] most of these are solids. The fluoro-substituted bis(dimethylamino)cyclotriphosphonitriles compound, Figure 7–4, is however, a liquid.

Bromine-containing phosphonitriles are of some interest due to the potential for fire extinguishment contribution by bromine and for possible synergism between bromine and phosphorus. The fully brominated compounds are solids or oils[99] and are, therefore, unlikely to be appropriate for investigation as fire extinguishants, though they may have other uses (e.g., flame retardants). Crown ether complexes have been used to prepare the highly colored solid compound NP_2Br_9 from KBr and hexachlorocyclotriphosphonitrile ($P_3N_3Cl_6$).[100] This compound can then be heated to form the more stable NP_2Br_7. Structures have not been published for either of these materials. The preparation of mixed fluorine- and bromine-substituted phosphonitriles by reaction of silver fluoride with $P_3N_3Br_6$ have been reported,[101] but the chemical and physical properties were not given.

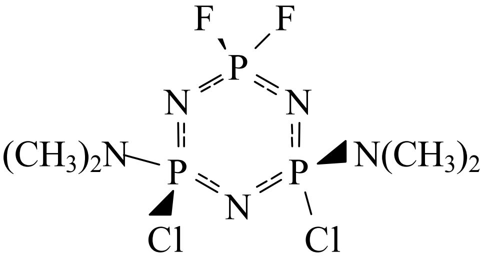


Figure 7–4. Example of a Fluoro-substituted Bis(dimethylamino) Cyclotriphosphonitrile.

Mixed methyl- and fluorine-substituted phosphonitriles have been prepared by reaction of octafluorocyclotetraphosphonitrile with methyl lithium.[102,103] The compounds are high boiling liquids and solids. Derivatives with tert-butyl and n-butyl substituents[104,105] and with 1- and 2-propenyl substituents[106] have also been reported.

Acquired phosphonitriles were reported to have attractively low cup burner flame extinguishment concentrations (Table 7–16).[93] The first of these compounds was even more efficient at extinguishing an opposed flow diffusion flame.[3] A number of polyfluoroalkoxy-substituted compounds (e.g., $P_3N_3(OCH_2CF_3)_6$) have also shown very good extinguishments characteristics.

Table 7–16. Phosphonitrile Flame Extinguishment

Chemical Formula	Cup Burner Extinguishing (volume %)
$P_3N_3F_6$	1.08 ± 0.07
$P_3N_3ClF_5$	0.91 ± 0.02
$P_3N_3Cl_2F_4$	0.96 ± 0.08

Phosphoranes

A number of fluorophosphoranes (pentacoordinate phosphorus(V) compounds), including some amino-substituted products have been described.[107,108] Although all of these contain phosphorus-fluorine bonds (making them unlikely candidates as halon replacements), the boiling points are in the acceptable range for a number of compounds. Unfortunately, none of the alkyl derivatives in the sources cited was fluorinated.

Phosphorus Halides

As shown in Table 7–17, some of these compounds are four to eight times as efficient as halon 1301 as flame suppressants. However, the boiling points are too high for aircraft use, except perhaps PF_3. Moreover, the toxicity and corrosiveness of these compounds is expected or known to be high. Nonetheless, it would be useful to examine the possibly more stable, totally fluorinated compounds, PF_3 and $O=PF_3$.

Table 7–17. Phosphorus Halide Flame Extinguishment.

Chemical Formula	T_b (°C)	Efficiency Relative to Halon 1301
PCl_3	75	6.7, 6.9
PBr_3	173	4.6, 6.9
PF_2Br	23.9	
PF_3	16.5	
$O=PCl_3$	34.4	5.2
$O=PF_2Br$	32	
$S=PCl_3$		8
$S=PBr_3$		6.7, 6.9

Phosphorus-containing Compounds – Atmospheric Lifetime, ODP, and GWP

The effect of phosphorus on stratospheric ozone has not been reported. A general cycle that may enable ozone depletion by phosphorus is shown in Reactions 7-13 and 7-14. Note, however, that the large stability and expected reluctance to add additional oxygen atoms make $\bullet PO_3$ and higher oxides unlikely candidates for direct participation in ozone depletion. $\bullet NO_3$ is known to photolyze sufficiently rapidly that at least some possible reactions are believed to be insignificant in atmospheric chemistry, and the higher oxides of phosphorus are likely to photolyze even more rapidly.[109]

$$\bullet PO_x + O_3 \rightarrow \bullet PO_{x+1} + O_2 \qquad (7\text{-}13)$$

$$\bullet PO_{x+1} + \bullet O \rightarrow PO_x + O_2 \qquad (7\text{-}14)$$

Nitrogen oxides are believed to deplete stratospheric ozone by the reactions shown in Reactions 7-15 through 7-17.[110] Here and elsewhere in this chapter, enthalpies of reaction (ΔH_r) and free energies of reaction (ΔG_r) were calculated from standard enthalpies of formation (ΔH_f) and standard free energies of formation (ΔG_f) at 298.15 K taken from Reference 111 unless otherwise indicated. By analogy, one might propose Reactions 7-18 and 7-19 for ozone depletion by phosphorus. Reaction 7-18 is highly exothermic and has been proposed as the cause for the chemiluminescence observed for the reaction of ozone with phosphine.[112] Here, however, the relatively large O-PO bond dissociation enthalpy (calculated as 540 kcal/mol from the standard enthalpies) compared to the O-NO bond dissociation energy (306 kJ/mole) makes the second reaction in the cycle (Reaction 7-19) unfavorable at 298.15 K. The higher stability of phosphorus dioxide can be seen from the total enthalpy of 1129 kJ/mole for dissociation of PO_2 into its constituent atoms compared with the calculated value of 938 kJ/mole for NO_2.

$$\bullet NO + O_3 \rightarrow \bullet NO_2 + O_2,\ \Delta H_r = -200\text{ kJ/mole},\ \Delta G_r = -199\text{ kJ/mole} \qquad (7\text{-}15)$$

$$\bullet NO_2 + \bullet O \rightarrow \bullet NO + O_2,\ \Delta H_r = -192\text{ kJ/mole},\ \Delta G_r = -196\text{ kJ/mole} \qquad (7\text{-}16)$$

$$\text{Net: } \bullet O + O_3 \rightarrow 2O_2,\ \Delta H_r = -392\text{ kJ/mole},\ \Delta G_r = -395\text{ kJ/mole} \qquad (7\text{-}17)$$

$$\bullet PO + O_3 \rightarrow \bullet PO_2 + O_2,\ \Delta H_r = -435\ kJ/mole,\ \Delta G_r = -433\ kJ/mole \qquad (7\text{-}18)$$

$$\bullet PO_2 + \bullet O \rightarrow \bullet PO + O_2,\ \Delta H_r = 42\ kJ/mole,\ \Delta G_r = 38\ kJ/mole \qquad (7\text{-}19)$$

An alternative mechanism is described in Reactions 7-20 and 7-21, where the second reaction is again distinctly unfavorable. This cycle is similar to the chlorine ozone depletion cycle in Reactions 7-22 and 7-23. Here, again, the large phosphorus-oxygen bond strength is an obstacle. The bond strength in diatomic PO is 599.1 kJ/mole compared with 269 kJ/mole for •ClO.[58]

$$\bullet P + O_3 \rightarrow \bullet PO + O_2,\ \Delta H_r = -483\ kJ/mole,\ \Delta G_r = -490\ kJ/mole \qquad (7\text{-}20)$$

$$\bullet PO + \bullet O \rightarrow \bullet P + O_2,\ \Delta H_r = 91\ kJ/mole,\ \Delta G_r = 95\ kJ/mole \qquad (7\text{-}21)$$

$$\bullet Cl + O_3 \rightarrow \bullet ClO + O_2,\ \Delta H_r = -163\ kJ/mole,\ \Delta G_r = -171\ kJ/mole \qquad (7\text{-}22)$$

$$\bullet ClO + \bullet O \rightarrow \bullet Cl + O_2,\ \Delta H_r = -229\ kJ/mole,\ \Delta G_r = -224\ kJ/mole \qquad (7\text{-}23)$$

Bromine and chlorine jointly provide a highly effective mechanism for stratospheric ozone depletion through a cycle of Reactions 7-17 and 7-24 through 7-26.[113] Here, ΔH_f and ΔG_f for •BrO were taken from Reference 58. A similar cycle can be proposed for phosphorus by coupling Reactions 7-20, 7-24, and 7-27. The free energy change for Reaction 7-27, however, is very large, positive, and, thus, unfavorable.

$$\bullet Br + O_3 \rightarrow \bullet BrO + O_2,\ \Delta H_r = -129\ kJ/mole,\ \Delta G_r = -137\ kJ/mole \qquad (7\text{-}24)$$

$$\bullet ClO + \bullet BrO \rightarrow \bullet Cl + \bullet Br + O_2,\ \Delta H_r = 6\ kJ/mole,\ \Delta G_r = -18\ kJ/mole \qquad (7\text{-}25)$$

$$\text{Net: } 2O_3 \rightarrow 3O_2,\ \Delta H_r = -285\ kJ/mole,\ \Delta G_r = -326\ kJ/mole \qquad (7\text{-}26)$$

$$\bullet PO + \bullet BrO \rightarrow \bullet P + \bullet Br + O_2,\ \Delta H_r = 326\ kJ/mole,\ \Delta G_r = 301\ kJ/mole \qquad (7\text{-}27)$$

The analysis presented above provides a strong indication that any ozone depletion must involve reaction of O_3 with •PO (e.g., Reactions 7-18 and 7-19). The phosphorus-oxygen bond in this diatomic molecule is too strong to allow formation of significant concentrations of atomic phosphorus. As noted above, however, the second reaction in the cycle (Reaction 7-19) is unfavorable at 298.15 K. The minimum stratospheric temperature (at the tropopause) varies from approximately 193 K to 223 K depending on the latitude, and the maximum stratospheric temperature (at the mesopause) is approximately 285 K depending on the season and latitude.[114] Data from the JANAF tables[111] indicate that the reaction becomes even less favorable (ΔH_r and ΔG_r both become more positive) as the temperature decreases from 298.15 K. A major question is how fast •PO is removed by reaction with O_3 (Reaction 7-18) before it reacts with O_2 (the reverse of Reaction 7-19). Ozone concentrations vary widely in the stratosphere; however, we can take the concentration of ozone in the stratosphere to be approximately

10^{10} molecules/cm^3 to 10^{11} molecules/cm^3 compared to a maximum of around 10^9 molecules/cm^3 for •O(^{3}P).[i,115,116] Thus, the mixing ratio (the ratio to air) for •O(^{3}P) is calculated as approximately 1 µL/L in the stratosphere. This implies that Reaction 7-19 would lie far to the left and that the concentration of •PO would be small.

Missing, of course, from this analysis is an assessment of kinetics for Reactions 7-18 and 7-19. Also missing is any discussion of other reactions of •PO and •PO_2, both of which are highly polar and are likely to be absorbed onto ice crystals. Despite the shortcomings of this analysis, it is obvious that stratospheric ozone depletion by phosphorus-containing compounds is very unlikely.

Relatively few data are available on atmospheric lifetimes for phosphorus compounds. Atkinson has reported the rate constants for several phosphorus compounds,[117] and these are shown in Table 7–18 along with atmospheric lifetimes estimated from the globally averaged tropospheric •OH concentration. Very limited data indicate that the presence of a phosphorus atom increases •OH reactivity. Thus, for example, methane (CH_4) has a rate constant of 0.0836×10^{-12} cm^3/molec-s at 298 K,[117] a value considerably smaller than that found for phosphine (PH_3), even though methane has one more reactive site (i.e., one more hydrogen atom). The activation energy for hydrogen atom abstraction decreases (as expected) with decreasing dissociation energy of the M-H bond, and this undoubtedly explains the higher rate constant for PH_3 (bond strengths: H-PH_2, 351.0 kJ/mol; C-CH_3, 438.9 kJ/mol).[58,118,119] It is difficult to compare compounds with and without phosphorus and containing hydrogen bonded only to carbon, since there are no isostructural compounds. The rate constant of 3.92×10^{-12} cm^3/molec-s at 298 K for 2,2-dimethoxypropane ($C(CH_3)_2(OCH_3)_2$) is smaller than that of trimethylphosphate ($(CH_3O)_3PO$), which has three fewer hydrogen atoms. The rate constant of 11.7×10^{-12} cm^3/molec-s at 298 K for 2,2-diethoxypropane ($C(CH_3)_2(OC_2H_5)_2$) is smaller than that of triethyl phosphate ($(C_2H_5O)_3PO$), which has nearly the same number of hydrogen atoms.[117] Since the predominant mechanism for reaction with the compounds in Table 7–18 appears to be hydrogen atom abstraction[117] it may be that a decreased bond strength accounts for the possibly higher reactivity for phosphorus-containing compounds; however, bond strength data to confirm this are lacking.

Table 7–18. Rate Constants •OH Reactions With Phosphorus Compounds.

Chemical Formula	k_2 at 297 K, cm^3/molec-s	Estimated Tropospheric Lifetime, days
PH_3	$13 \pm 3 \times 10^{-12}$	0.9
$(CH_3O)_3PO$	$7.37 \pm 0.74 \times 10^{-12}$	1.6
$(C_2H_5O)_3PO$	$55.3 \pm 3.5 \times 10^{-12}$	0.2
$(CH_3O)_2P(O)SCH_3$	$9.29 \pm 0.68 \times 10^{-12}$	1.3
$(CH_3S)_2P(O)OCH_3$	$9.59 \pm 0.75 \times 10^{-12}$	1.2
$(CH_3O)_3PS$	$69.7 \pm 3.9 \times 10^{-12}$	0.2
$(CH_3O)_2P(S)SCH_3$	$56.0 \pm 1.8 \times 10^{-12}$	0.2
$(CH_3O)_2P(O)N(CH_3)_2$	$31.9 \pm 2.4 \times 10^{-12}$	0.4
$(CH_3O)_2P(S)N(CH_3)_2$	$46.8 \pm 1.4 \times 10^{-12}$	0.3
$(CH_3O)_2P(S)NHCH_3$	$233 \pm 15 \times 10^{-12}$	0.05
$(CH_3O)_2P(S)NH_2$	$244 \pm 9 \times 10^{-12}$	0.05
$(CH_3O)_2P(S)Cl$	$59.0 \pm 3.8 \times 10^{-12}$	0.2

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[i] The concentration of oxygen atoms in other than the ^{3}P ground state would be even smaller.

Phosphorus compounds studied to date are quite unreactive toward ozone. An upper limit of 6×10^{-20} cm^3/molecules has been determined for reaction of trimethylphosphate ($(CH_3O)P=O$) with ozone at 296 K.[120] Using a globally averaged tropospheric ozone concentration, one estimates from this value a minimum lifetime of 386 days for reaction of trimethylphosphate with tropospheric ozone. Atkinson has reported rate constants with upper limits on the order of 10^{-19} at 296 K to 298 K for gas-phase reactions of O_3 with phosphorus-containing compounds, giving estimated minimum lifetimes of around 200 days. In none of these cases was a reaction observed.[121]

It is likely that many phosphorus compounds are sufficiently polar that rainout is an important tropospheric removal mechanism. Atmospheric hydrolysis is possible for phosphonitriles containing direct P-halogen bonds even when the halogen is fluorine, and this is likely to be an effective tropospheric removal mechanism for such compounds. Photolysis is more important for compounds containing phosphorus than for corresponding carbon compounds; however, insufficient data are available to determine whether photolysis provides effective atmospheric removal.

No rigorous calculations of atmospheric lifetimes or GWPs of phosphorus-containing compounds have been reported. A 3 day lifetime has been estimated for trimethylphosphate based on the rate constant for reaction with •OH.[120] This value differs slightly from that given in Table 7–18 due to the use of a slightly different globally averaged •OH.

In summary, phosphorus compounds are unlikely sources of stratospheric ozone depletion due to the presence of phosphorus only. When hydrogen atoms are present, limited data indicate effective removal by tropospheric •OH and short atmospheric lifetimes. Insufficient data are available to judge tropospheric removal and atmospheric lifetimes for phosphorus compounds containing no hydrogen; however, it is likely that rainout and/or hydrolysis will give short atmospheric lifetimes. In summary, there is no evidence to suggest that phosphorus compounds will have unacceptable global atmospheric environmental properties (i.e., unacceptable ODP, GWP, or lifetime).

Toxicity of Phosphonitrilic Compounds

A general review of the toxicity of phosphorus compounds is also accessible in Reference 93. One concern is that a number of phosphorus compounds (particularly phosphite esters) are cholinesterase inhibitors. The following summarizes results from tests of this particular class of compounds.

Hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene toxicity: An acute oral toxicity assessment utilizing male and female Fischer 344 rats and genotoxicity testing utilizing the Ames assay has been performed on hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene ($P_3N_3(OCH_2CF_3)_6$).[122] No deaths or signs of toxic stress were observed in any of the rats orally dosed at the limit test value of 5 g of $P_3N_3(OCH_2CF_3)_6$ per kg body weight. Body weights of the male rats during the subsequent 14 day observation period appeared unaffected by treatment. In the Ames assay, $P_3N_3(OCH_2CF_3)_6$ produced no mutagenicity (base-pair substitution or frameshift mutation) in the bacterial (Salmonella) system. In summary, $P_3N_3(OCH_2CF_3)_6$ produced no toxicity via the oral route of administration and was determined not to be genotoxic.

Phosphonitrilic Chloride Compounds (Chlorophosphazene): In 1979, Ethyl Corporation submitted to the U. S. Environmental Protection Agency (EPA) the results of in vitro and in vivo studies on two similar phosphonitrilic chloride compounds, each with the same CAS (Chemical Abstracts Service) No. (25034-79-1). In all, there were 16 reports, each covering a separate toxicological test for each compound:

a. *In vitro* mammalian cell transformation assay.[123,124]

b. *In vitro* mammalian cell transformation assay in the presence of exogenous metabolic activation assay.[125,126]

c. *In vivo* mammalian cell point mutation assay.[127,128]

d. *In vitro* mammalian cell point mutation assay in the presence of exogeneous metabolic activation assay.[129,130]

e. *In vivo* cytogenetic assay in rodents for mutagenicity.[127]

f. *Salmonella*/Microsomal assay for bacterial mutagenicity assay.[131,132]

g. Differential inhibition of repair deficient and repair competent strains of *Escherichia Coli*: DNA (deoxyribonucleic acid) repair assay.[133,134]

h. Dominant lethal assay in rodents for mutagenicity assay.[135,136]

Table 7–19 paraphrases the results of the eight toxicity tests for each compound. Due to the limited solubility of the test compounds in vehicles compatible with mammalian cell culture systems, it was difficult to establish the exact concentration of the chemical in solution for the *in vitro* tests, a problem noted in the reports cited.

Table 7–19. Toxicity Studies of Chlorophosphazenes.

3899-A	3899-B
***In Vitro* Mammalian Cell Transformation Assay**	
a. Although the cytotoxicity tests were not reproducible in showing the toxic effects of the test compound with target cells, a dose response effect was observed in each of the cytotoxicity studies. b. The test compound was incapable of inducing morphological transformants (Type III foci) in the BALB/3T3 clone A31 cell system.	a. The cytotoxicity studies demonstrated a dose response effect. b. The test chemical was demonstrated to be positive in producing a Type III foci at 60 µg/mL concentration. Relative to solvent (acetone), the number of morphologically transformed (Type III) foci present at this concentration was statistically significant ($P<0.05$).
***In vitro* Mammalian Cell Transformation Assay in the Presence of Exogenous Metabolic Activation**	
a. Cytotoxic effects of the test agent appeared to increase in the presence of an exogeneous source of metabolizing activity (S-9). b. The test chemical was effective in inducing morphological transformation (Type III foci) at the 30 µg/mL concentration. Relative to the negative control, the number of morphologically transformants per number of cells at risk at the 30 µg/mL concentration was not statistically significant ($P>0.05$).	a. Cytotoxic effects of the test agent appeared to increase in the presence of an exogeneous source of metabolizing activity (S-9). b. The test chemical was effective in inducing morphological transformation (Type III foci) in the BALB/3T3 Clone A31 cell system at all concentrations employed.
***In Vitro* Mammalian Cell Point Mutation Assay**	
a. Although the cytotoxicity tests were not reproducible in showing the toxic effects of the test compound with target cells, a dose response effect was observed in each of the cytotoxicity studies. b. The test compound was incapable of inducing ouabain-resistant colonies at all of the doses tested.	a. The cytotoxicity tests demonstrated a dose response effect. b. The test chemical was incapable of inducing ouabain-resistant colonies at all concentrations.

3899-A	**3899-B**
***In Vitro* Mammalian Cell Point Mutation Assay with Exogenous Metabolic Activation**	
a. Cytotoxic effects of the test agent appeared to increase in the presence of an exogenous source of metabolizing activity (S-9). b. The test chemical was ineffective in inducing ouabain-resistant colonies in the BALB/3T3 Clone A31 cell system at all concentrations employed.	a. The cytotoxic effects of the test agent appeared to increase in the presence of an exogenous source of metabolizing activity (S-9). b. The test chemical was ineffective in inducing ouabain-resistant colonies at all concentrations employed.
***In Vitro* Cytogenetic Assay in Rodents for Mutagenicity**	
The test compound exhibited little or no clastogenic activity. No dose response was observed. Under the conditions of this test, the data suggest that the test compound exhibits little or no mutagenic activity.	The test compound exhibited moderate clastogenic activity. A dose response was observed. Under the conditions of this test, the data suggest that the compound exhibits mutagenic activity.
Dominant Lethal Assay in Rodents for Mutagenicity	
Test compound appeared to exhibit minimal activity in total implantations, number of live implantations per pregnant female, and pre-implantation losses. No significant dose response was observed and little or no mutagenic activity in the dominant lethal test.	Test compound appeared to exhibit minimal activity in total implantations, number of live implantations per pregnant female, and pre-implantation losses. No significant dose response was observed and little or no mutagenic activity in the dominant lethal test.
***Salmonella*/Microsomal Assay for Bacterial Mutagenicity**	
a. The test agent did not induce a significant increase in the number of point mutations in *Salmonella* typhimurium strains in the absence of activating system for strains TA1535, TA1537, TA1358, TA100, and TA98. b. It did not induce a significant increase in the number of point mutations with the addition of an exogenous source of liver enzymes for metabolic activation in strains of TA1535, TA1537, TA1358, TA100, and TA98.	a. Test agent did not induce significant increase in number of point mutations in *Salmonella* typhimurium strains in the absence of activating systems for TA1535, TA1537, TA100, TA98. b. Induced a significant increase in the number of point mutations in the absence of the activating system for strain TA1538. c. Did not induce a significant increase in the number of point mutations with the addition of an exogenous source of liver enzymes for activation.
Differential Inhibition of Repair Deficient and Repair Competent Strains of *Escherichia Coli* (*E. coli*): DNA Repair	
The test chemical did not produce a statistically significant difference in its ability to produce cell death between repair deficient (polA$^-$) and repair competent (polA$^+$) strains in *E. coli*.	Test chemical produced statistically significant difference at 2 µL per plate in production of cell death between repair deficient (polA$^-$) and repair competent (polA$^+$) strains in *E. coli*.

The fact that a positive effect was obtained in a number of *in vitro* tests indicates that the material may be a potential mutagen, and thus this class of materials may be mutagenic. Note that compound 3899-B (the less refined compound) generally appeared more toxic. This indicated that impurities and other chemicals may increase toxicity to an unacceptable level even if the pure compounds are not unacceptably toxic.

Other Phosphorus Compounds: In a study of a number of phosphorus compounds, no toxic signs were observed following 15 6 h exposures of two male and two female rats to 200 µL/L tributyl phosphite, $P(OC_4H_9)_3$.[137] The blood, urine, and organs (upon autopsy) were normal. The same study showed that tris(hydroxymethyl)propane bicyclic phosphite, Figure 7–5, has an unexpectedly high toxicity and was stated to be "one of the most toxic compounds handled in this laboratory." All rats died following a 1 h exposure to 10 µL/L. The action on the central nervous system was probably due to its sufficient stability to penetrate cell membranes as a non-ionized molecule, possibly with subsequent hydrolysis. Note, however, that its hydrolysis product, dihydroxybutylphosphonic acid, has a low oral and parental toxicity.

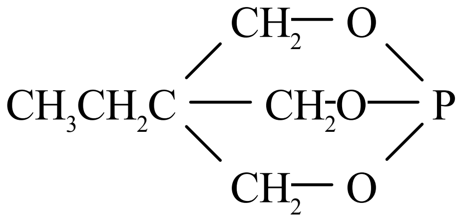


Figure 7–5. Tris(hydroxymethyl)propane Bicyclic Phosphite.

Phosphorus Tribromide (PBr_3)

In spite of its contact toxicity and corrosive hazards, documented in material safety data sheets[67,138], the attraction of a reactive molecule containing four catalytic atoms (three bromine atoms and a phosphorus atom) led to several studies of the efficacy of phosphorus tribromide (PBr_3) molecule as a fire extinguishant.[84,85,92] The high boiling point (173 °C) and low vapor pressure (1.3 kPa @ 48 °C) of PBr_3 indicated that in fire suppression applications the compound would have no dimensionality, and unless the compound were applied in sufficient quantity directly on the burning surface, it was unlikely that complete and reliable flame extinguishment would be obtained. These physical properties led to the conclusion that PBr_3 had no promise as a total flooding agent. The alternative study of low boiling bromine carriers such as the alkenes and ethers was judged more likely to yield a more toxicologically and environmentally acceptable halon replacement with greater dimensionality, and therefore no further effort to study PBr_3 was made.

Nonetheless, studies continued. In the 1990s, there were limited press releases of some studies of PBr_3, along with poster session presentations at the annual Halon Options Technical Working Conferences in the 1990s. A report to the Air Force conveyed some technical documentation.[139]

Recently, it was announced that a commercial aircraft engine nacelle fire extinguishment system would employ this chemical, in very small quantity relative to halon 1301.[140] The described approach utilized focusing a spray of the PBr_3 onto a location where the fire was assumed to occur. This approach gained its advertised agent mass and volume advantage because halon 1301 is typically discharged to flood the entire engine nacelle. Total flooding mitigates the risk that the fire might start in an obstructed location and not be extinguished. In addition, the discharge of HFCs and halons is accompanied by significant cooling of hot surfaces in and around the flame zone. This is credited with diminishing or even eliminating the potential for relight of hot liquids and vapors present in the burn zone. There was no presentation of same-test-fixture comparison of the PBr_3 system to halon 1301 extinguishment.

Arsenic, Bismuth, and Antimony

Antimony has been extensively used in flame retardants, usually in conjunction with bromine-containing compounds.[48] No studies on fires suppression by arsenic or bismuth compounds have been found. Arsenic and antimony compounds are too toxic to meet that screening criterion.

7.3.6 Main Group Elements - Group VI

Oxygen

Oxygen compounds are included under other headings and are not covered here. The use of water (H_2O) as an extinguishant dates to before the earliest historical written records. There is no indication that simple inorganic oxygen compounds provide any type of catalytic fire suppression capability.

Sulfur

A sulfur dioxide cycle (Reactions 7-28 and 7-29) has been proposed to inhibit combustion by removal of hydrogen atoms.[79]

$$H + SO_2 + M \rightarrow HSO_2 + M^* \qquad (7\text{-}28)$$

$$H + HSO_2 \rightarrow H_2 + SO_2 \qquad (7\text{-}29)$$

However, no fire suppression tests have been conducted on these compounds, and there is no evidence indicating that the sulfur atom imparts any chemical fire suppression capability. The nonhalogenated sulfur-containing compounds are generally flammable. Thus, attention was directed at highly halogenated compounds.

It appeared possible that brominated fluorosulfur compounds could be efficient fire suppressants and have short atmospheric lifetimes. However, no affordable sources of these compounds could be located, and there was also expectation that their volatility would be insufficient.

The perfluoroalkyl sulfur compounds have relatively high oxidation and hydrolysis stability. Bis(trifluoromethyl)sulfide (CF_3-S-CF_3) is prepared by heating bis(trifluoromethyl)disulfide (CF_3-SS-CF_3) at 425 °C for 3 days to 4 days.[141] This and other perfluoroalkylsulfides can also be prepared by heating or photolysis of $R_fOC(O)R_f$, where R_f is a perfluoroalkyl group.[142,143] The ester is prepared by reaction of R_f -S-Cl and silver perfluorocarboxylates ($AgOOCR_f$). The derivatives R_f-SF_2-R_f, are prepared by fluorination of the corresponding sulfide with ClF or F_2, followed by hydrolysis to give R_f-S(O)-R_f[144,145] These compounds are generally hydrolytically and oxidatively stable.[141,143,144]

As can be seen in Table 7–20, only the first two sulfides are sufficiently volatile to meet the screening criterion for aircraft use.

A major drawback of sulfur compounds is the expected formation of toxic sulfur oxides or hydrogen sulfide during fire extinguishment. Toxicity concerns, a lack of availability of test chemicals, and likely long atmospheric lifetime of the fully fluorinated thioalkanes resulted in further examination of this family being abandoned.

Table 7–20. Perfluoroalkyl Sulfur Compounds.

Chemical Name	Formula	T_b (°C)
1,1,1,3,3,3-hexafluoro-2-thiopropane	CF_3-S-CF_3	[a]-22
1,1,1,3,3,4,4,4-octafluoro-2-thiobutane	CF_3-S-CF_2CF_3	[b]6.3
1,1,1,3,3,4,4,5,5,5-decafluoro-2-thiopentane	CF_3-S-$CF_2CF_2CF_3$	[b]38.6
1,1,1,2,2,3,3,3-octafluoro-2-thiopropane	$CF_3SF_2CF_3$	[b]21.0
1,1,1,2,2,3,3,4,4,4-decafluoro-2-thiobutane	$CF_3SF_2CF_2CF_3$	[b]44.1
1,1,1,2,2,3,3,4,4,5,5,5-dodecafluoro-2-thiopentane	$CF_3SF_2CF_2CF_2CF_3$	[b]69.3
1,1,1,2,2,3,3,4,4,5,5,6,6,6-dodecafluoro-3-thiopentane	$CF_3CF_2SF_2CF_2CF_3$	[b]69.5
1,1,1,3,3,3-hexafluoro-2-oxo-2-thiopropane	$CF_3S(O)CF_3$	[b]37.3
1,1,1,3,3,4,4,4-octafluoro-2-oxo-2-thiobutane	$CF_3S(O)CF_2CF_3$	[b]58.2
1,1,1,3,3,4,4,5,5,5-decafluoro-2-oxo-2-thiopentane	$CF_3S(O)CF_2CF_2CF_3$	[b]64.0

a Reference 141.
b Reference 143.

Selenium and Tellurium

The only compound containing one of these elements for which fire extinguishment capabilities have been reported is perfluoroselenolane.[146] There was no indication that selenium or tellurium compounds exhibited catalytic flame inhibition or that such compounds would have particular utility as halon replacements. Selenium toxicity was of great concern.[67,138]

7.3.7 Main Group Elements - Group VIII (Noble Gases)

Of the non-radioactive Group VIII elements (helium, neon, argon, krypton, and xenon), only xenon and, to a much lesser extent, krypton are known to form compounds. These compounds are strong oxidizing agents and would probably act to increase flame intensity rather than decrease it. At any rate, these are not stable at ordinary temperatures, so only the atoms would reach the flame. Like nitrogen, the noble gases extinguish flames by dilution and cooling. They thus did not meet the efficiency screening criterion.

7.3.8 Transition Metal Based Compounds

The 2001 NGP review[39] of the status of knowledge of fire suppressants recommended a further look at compounds of copper, iron, manganese, and tin. A more detailed and more current review (including extensive NGP research) of the chemistry of transition metal compounds appears in Chapter 3 of this book. That chapter notes data supporting high flame inhibition efficiency for a longer list of metals, adding chromium, cobalt, lead, molybdenum, and tungsten. Unfortunately, most metal-containing compounds from this larger set have the potential to lose their ability to quench flames due to condensation of the active species. There was no direct evidence for salts of cobalt, copper, molybdenum, and tungsten to lose their flame quenching potential.

All compounds containing these metals are solids or dense liquids at flight temperatures and are thus not sufficiently volatile for total flooding as gases. Thus, the NGP did not perform a systematic flame extinguishment study of these compounds. They could be dispensed by incorporation in a solid propellant fire extinguisher, as described in Chapter 9. The addition of K_2CO_3 has significantly improved the performance of a prototype device, and salts of these metals would need to be at least as beneficial for further consideration.

7.3.9 Inorganic Chemicals - Conclusions

Nearly all of the inorganic compounds are insufficiently volatile and/or have not shown even moderate fire suppression efficiency. They thus do not meet primary screening requirements for replacing halon 1301 in aircraft applications. A few compounds are moderately volatile, but are toxic or corrosive. Some phosphorus halides have boiling points that might be sufficient for use should the operational temperature criterion be raised significantly above the -40 ºC extreme at which halon 1301 alternatives are expected to perform.

7.4 NGP SURVEYS OF ORGANIC COMPOUNDS

7.4.1 Highly Efficient Thermal Agents

Screening

The NGP conducted extensive research to determine whether other organic compounds could be as efficient at flame extinguishment as halon 1301 simply by absorbing heat from the flames, i.e., without any chemical or catalytic activity.[147] A number of reports by Pitts et al. describe specific aspects of and the conclusions resulting from this research.[148,149,150,151,152,153,154] In this effort, two existing thermodynamic databases maintained by NIST were searched in order to identify chemical compounds predicted to extract large amounts of heat from a combustion zone:

- Design Institute for Physical Properties database (DIPPR), which contains 1458 compounds from 83 chemical families (Table 7–21) and
- REFPROP, which contains 43 compounds tailored to alternate refrigerant applications, including many candidates for replacing HCFCs.

This search also included representative compounds from some families of chemicals not well represented in existing thermophysical property databases. These were compounds having high heat of vaporization, liquid phase heat capacity, total heat absorption due to a phase change, and/or heat needed to raise the liquid or gas to combustion temperatures. Fluorinated ethers were important to consider, since their atmospheric lifetimes may be significantly lower than those of chlorofluorocarbons,[155] and some of these had been identified as possible replacements for blowing agents, refrigerants, fire suppression agents, and solvents.[21,156,157,158,159,160] Additional compounds were several cyclic fluorinated ether compounds (fluorinated oxiranes, oxetanes, and furans), some non-cyclic methyl ethers (HFE-116, HFE-125), fluorinated methyl ethyl ethers with two or fewer hydrogen atoms (HFE-227me, HFE-236me), and some larger fluorinated ethers (methoxy-nonafluorobutane, $C_4F_9OCH_3$, HFE-7100; perfluorodimethoxymethane, $CF_3OCF_2OCF_3$; perfluoropropyltrifluoromethyl ether, $CF_3OCF_2CF_2CF_3$; and heptafluoropropyl-1,2,2,2-tetrafluoroethyl ether, $CF_3CHFOCF_2CF_2CF_3$). Lastly, the list of compounds considered included two fluorinated amines, the alternative refrigerant HFC-338mccq ($CH_2FCF_2CF_2CF_3$), and the fluorinated alcohol 2,2,3,3,3-pentafluoropropanol ($CF_3CF_2CH_2OH$).

Table 7–21. Family Types in the DIPPR Database

#	Family Type	#	Family Type	#	Family Type
1	n-Alkanes	29	Cycloaliphatic alcohols	57	Other amines, imines
2	Methylalkanes	30	Aromatic alcohols	58	Nitriles
3	Dimethylalkanes	31	Polyols	59	C,H,NO2 compounds
4	Other alkanes	32	*n*-Aliphatic acids	60	Isocyanates/diisocyanates
5	Cycloalkanes	33	Other aliphatic acids	61	Mercaptans
6	Alkylcyclopentanes	34	Dicarboxylic acids	62	Sulfides/theophenes
7	Alkylcyclohexanes	35	Aromatic carboxylic acids	63	Polyfunctional acids
8	Multi-ring cycloalkanes	36	Anhydrides	64	Polyfunctional esters
9	1-Alkynes	37	Formates	65	Other polyfunctional C,H,O
10	2,3,4-Alkenes	38	Acetates	66	Polyfunctional nitriles
11	Methylalkenes	39	Propionates & Butyrates	67	Nitroamines
12	Ethyl and higher alkenes	40	Other saturated aliphatic esters	68	Polyfunc. amides/amines
13	Cycloalkenes	41	Unsaturated aliphatic esters	69	Polyfunctional C,H,O,N
14	Dialkenes	42	Aromatic esters	70	Polyfunctional C,H,O,S
15	Alkynes	43	Aliphatic ethers	71	Polyfunc. C,H,O,halides
16	n-Alkylbenzenes	44	Other ethers and diethers	72	Polyfunc. C,H,N,halides
17	Other alkylbenzenes	45	Epoxides	73	Other polyfunc. organics
18	Other monoaromatics	46	Peroxides	74	Elements
19	Napthalenes	47	C1/C2 aliphatic chlorides	75	Silanes/siloxanes
20	Other condensed rings	48	C3 & higher aliphatic chlorides	76	Organic-inorganic
21	Diphenyl/polyaromatics	49	Aromatic chlorides	77	Inorganic acids
22	Terpenes	50	C,H,Br compounds	78	Inorganic bases
23	Other hydrocarbon rings	51	C,H,I compounds	79	Organic salts
24	Inorganic gases	52	C,H,F compounds	80	Sodium salts
25	Aldehydes	53	C,H multihalogen compounds	81	Other inorganic salts
26	Ketones	54	*n*-Aliphatic primary amines	82	Inorganic halides
27	*n*-Alcohols	55	Other aliphatic amines	83	Other inorganics

The research approach involved developing a figure of merit for evaluating each compound based on the total enthalpy absorbed by the compound as it was heated from room temperature to flame temperature, represented by 1400 K. The total heat absorbed consists of three contributions (Equation 7-30),

$$\Delta H^{Total} = \Delta H_l + \Delta H_v + \Delta H_g \,, \qquad (7\text{-}30)$$

where the first contribtion, ΔH_l, is the heat involved in taking the liquid from room temperature up to the normal boiling point, T_b,

$$\Delta H_1 = \int_{298K}^{T_b} C_p^{liquid} \, \mathrm{d}T. \qquad (7\text{-}31)$$

The value of the liquid heat capacity (Equation 7-31) at the normal boiling point was used, since the heat capacity of a liquid does not change significantly over a small temperature range. If this was unavailable, the liquid phase heat capacity at 20 °C was estimated using the method of Chueh and Swanson.[161162]

The second term, ΔH_v, is the latent heat of vaporization at the normal boiling point. If not available, these were estimated using the approach of Fishtine.[163]

The third contribution, ΔH_g, is the integral, [Equation 7-32] of the gas-phase heat capacity from the normal boiling point to 1400 K,

$$\Delta H_g = \int_{T_b}^{1400K} C_p^{gas}\, \mathrm{d}T. \tag{7-32}$$

The gas phase heat capacities were estimated using the method of Rihani and Doraiswamy,[164] which was based on structural contributions. For agents with boiling points below 298 K, the total heat involved is just the contribution ΔH_v.

Table 7–22 summarizes the results of this computation, comparing the best of the examined chemicals, along with some reference compounds. The listing is in order of their ΔH^{Total} expressed on a molar basis (kJ/mol).

Table 7–22. Compounds with High ΔH^{Total} (Molar Basis).

	T_b (°K)	ΔH^{Total} (kJ/mol)
perfluoro-2-butyltetrahydrofuran, $C_8F_{16}O$	375.2	608.4
heptafluoropropyl-1,2,2,2-tetrafluoroethyl ether	315.2	421.9
methoxy-nonafluorobutane, HFE-7100	334	407.6
perfluoropropyltrifluoromethyl ether,$CF_3OCF_2CF_2CF_3$	279.9	336.3
perfluoroisobutane, C_4F_{10}	252.5	321.2
1,1,1,2,2,3,3,4-octafluorobutane, HFC-338mccq	301	321.0
decafluorobutane, C_4F_{10}	271	318.5
octafluorocyclobutane, C_4F_8	267	303.2
perfluorotrimethylamine, C_3F_9N	264	293.8
lactic acid, $C_3H_6O_3$	455	292.9
perfluorodimethoxymethane, $CF_3OCF_2OCF_3$	263	286.8
octafluorofuran, C_4F_8O	272.4	289.8
2,2,3,3,3-pentafluoropropanol, $C_3F_5H_3O$	353.15	280.8
octafluoro-2-butene	270	261.9
tris(difluoromethyl)amine, $C_3H_3F_6N$	275	256.5
trifluoromethyl-1,2,2,2-tetrafluoroethyl ether, HFE-227me	263.6	255.3
octafluoropropane, FC-218	236.4	250.8
difluoromethyl-1,2,2,2-tetrafluoroethyl ether, HFE-236me	296.5	239.4
1,1,1,2,3,3,3-heptafluoropropane, HFC-227ea	257.5	236.5
1,1,1,2,3,3-hexafluoropropane, HFC-236ea	279.7	222.2
bis(trifluoromethyl)ether, HFE-116	257	196.2
pentafluorodimethylether, HFE-125	235	183.8
hexafluoroethane, FC-116	194.95	181.1
1,1,2,2-tetrafluorodimethylether, HFE-134	279.4	170.2
pentafluoroethane, HFC-125	**225.2**	**166.8**
1,1,1,2-tetrafluoroethane, HFC-134a	247	156.8
1,1,2,2-tetrafluoroethane, HFC-134	250	152.8
bromotrifluoromethane, halon 1301	**215.26**	**110.9**
Water, H_2O	373.1	87.5
carbon dioxide, CO_2	N/a	56.2
Nitrogen, N_2	77.4	34.7
Argon, Ar	87.3	22.9

Table 7–23 gives the same quantity, but expressed on a mass basis (kJ/kg). Compounds that were identified as flammable or toxic, or that had known ozone depletion problems, have been eliminated. The DIPPR database does not contain any information on toxicity or other health effects. This information came from manufacturers' safety data sheets and Hawley.[165] Since the information on toxicity was incomplete, further investigation of some chemicals would be needed. The web site at http://chemfinder.camsoft.com/ provided OPD and GWP information. Perfluorocarbons are included for reference, although the EPA has indicated they may be used only when all other compounds are inappropriate. Halon 1301 and HFC-125, two reference compounds, are shown in boldface.

Table 7–23. Compounds with High ΔH^{Total} (Mass Basis).

Chemical Name, Formula	T_b (°K)	ΔH^{total} (kJ/kg)
Water, H_2O	373.1	4855.7
lactic acid, $C_3H_6O_3$	455	3251.6
2,2,3,3,3-pentafluoropropanol, $C_3F_5H_3O$	353.15	1872.0
methoxy-nonafluorobutane, HFE-7100	334	1630.4
1,1,1,2,2,3,3,4-octafluorobutane, R338mccq	301	1588.7
1,1,1,2-tetrafluoroethane, HFC-134a	247	1536.8
tris(difluoromethyl)amine, $C_3H_3F_6N$	275	1535.5
octafluorocyclobutane, C_4F_8	267	1515.8
1,1,2,2-tetrafluoroethane, HFC-134	250	1497.6
heptafluoropropyl-1,2,2,2-tetrafluoroethyl ether	315.2	1475.0
perfluoro-2-butyltetrahydrofuran, $C_8F_{16}O$	375.2	1462.3
1,1,1,2,3,3-hexafluoropropane, HFC-236ea	279.7	1461.4
1,1,2,2-tetrafluorodimethylether, HFE-134	279.4	1442.0
difluoromethyl-1,2,2,2-tetrafluoroethyl ether, HFE-236me	296.5	1424.7
1,1,1,2,3,3,3-heptafluoropropane, HFC-227ea	257.5	1390.9
pentafluoroethane, HFC-125	**225.2**	**1389.8**
trifluoromethyl-1,2,2,2-tetrafluoroethyl ether, HFE-227me	263.6	1372.4
pentafluorodimethylether, HFE-125	235	1351.3
perfluoroisobutane, C_4F_{10}	252.5	1349.6
octafluorofuran, C_4F_8O	272.4	1341.5
decafluorobutane, C_4F_{10}	271	1338.2
octafluoropropane, FC-218	236.4	1333.8
perfluorotrimethylamine, C_3F_9N	264	1329.3
perfluoropropyltrifluoromethyl ether, $CF_3OCF_2CF_2CF_3$	279.9	1323.9
hexafluoroethane, FC-116	194.95	1312.2
octafluoro-2-butene	270	1309.2
perfluorodimethoxymethane, CF3OCF2OCF3	263	1303.5
carbon dioxide, CO2	n/a	1276
bis(trifluoromethyl)ether, HFE-116	257	1273.9
nitrogen, N2	77.4	1238.3
bromotrifluoromethane, halon 1301	215.26	744.7
Argon, Ar	87.3	573.2

The results of Table 7–22 indicate that the top candidates for use in moderate (ground level) ambient temperature environments or as streaming agents (defined here as having boiling points higher than 293 K), on a molar basis, are perfluoro-2-butyltetrahydrofuran, methoxy-nonafluorobutane, heptafluoropropyl-1,2,2,2-tetrafluoroethyl ether, and 1,1,1,2,2,3,3,4-octafluorobutane.

Table 7–23 indicates that methoxy-nonafluorobutane (HFE-7100) is also high on the list when expressed on a mass basis. It is available commercially.[166] The others are not, but have been synthesized and used for research.[167, 168,169] The top total-flooding candidates (defined as having boiling points lower than 293 K) are perfluoropropyltrifluromethyl ether, perfluoroisobutane, decafluorobutane, and octafluorocyclobutane. Of these, the last two are available commercially.[170] The latter three are perfluorocarbons and thus not reasonable to consider further.

HFE-7100 was developed as a replacement for ozone-depleting chemicals used in a variety of applications. It has been estimated to have a zero ozone depletion potential, a relatively low global warming potential, low toxicity, and good materials compatibility.[166] It has been approved under the Significant New Alternatives Policy (SNAP) of the United States Environmental Protection Agency. There is an existing patent dealing with use of HFE-7100 as a fire-extinguishing agent. Based on these favorable properties, it was decided to characterize the extinguishing capability of HFE-7100 experimentally.

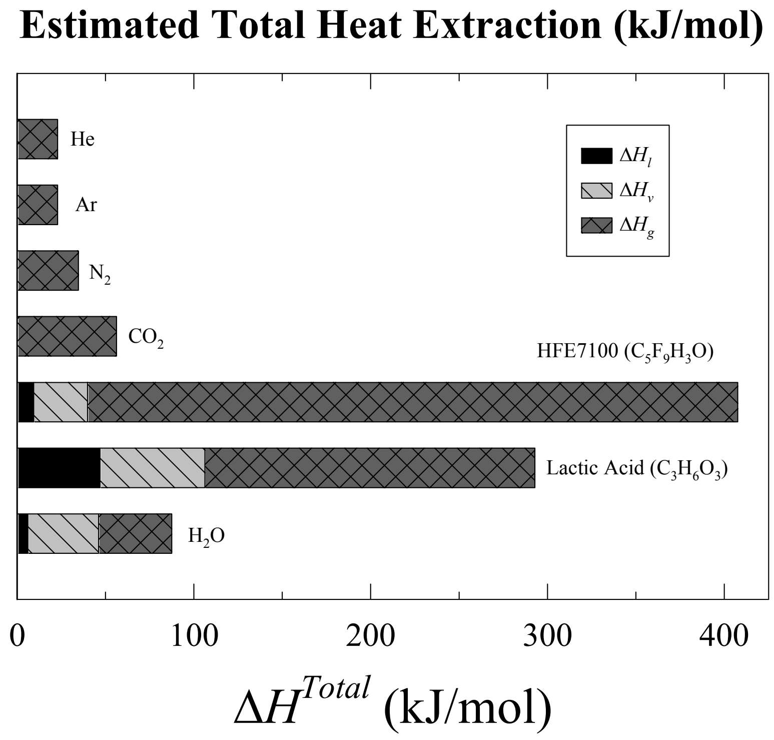
The data included in Table 7–23 indicate that lactic acid is predicted to be highly effective as a thermal agent. Clearly, this compound is not a potential candidate as a replacement for halon 1301 for in-flight fires due to its high boiling and melting points and caustic nature. It is also an organic compound and may be combustible. However, based solely on its ability to extract heat, it is predicted to be nearly twice as effective on a mass basis as any of the other potential thermal agents considered, except water. Its ability to extract heat is predicted to be roughly two-thirds of that of water on a mass basis and 3.5 times greater on a molar basis. Since lactic acid is soluble in water, it was deemed worthwhile to investigate the suppression characteristics of mixtures of these two polar liquids.

Effectiveness of Thermal Agents

In order to understand the effectiveness of thermal agents better, experimental and modeling investigations were performed for flame extinguishment by water, lactic acid, and HFE-7100. Prefatory measurements and calculations for simpler, gaseous thermal agents (nitrogen, carbon dioxide, argon, and helium) were used to establish the viability of the approach.[147]

Figure 7–6 shows the relative contributions of the various heat extraction mechanisms in Equation 1 for the seven agents in terms of heat extraction per mole of agent and per mass of agent. On a molar basis HFE-7100 is predicted to be the most effective, with lactic acid a close second. The contribution of liquid processes to the total heat extraction is relatively small for HFE-7100. Liquid water is predicted to be the next most effective due primarily to the relatively high heat absorbed during evaporation. The four gaseous agents are predicted to be relatively ineffective and are ordered $CO_2 > N_2 > Ar = He$.

On a per mass basis, the plot has a very different appearance. The most effective agent in these terms is helium followed by water and lactic acid. On this plot the role of heat extraction by heating and vaporization of the liquid agents is clear. It can be seen that for water, over half of the heat extraction arises from the liquid processes. For lactic acid, the contribution of liquid vaporization to the total heat extraction is significant, but greatly reduced as compared to water. The large differences between the HFE-7100 and lactic acid and water are due to hydrogen bonding that exists in water and lactic acid. This bonding significantly increases the amount of heat energy required to vaporize liquids when it is present.



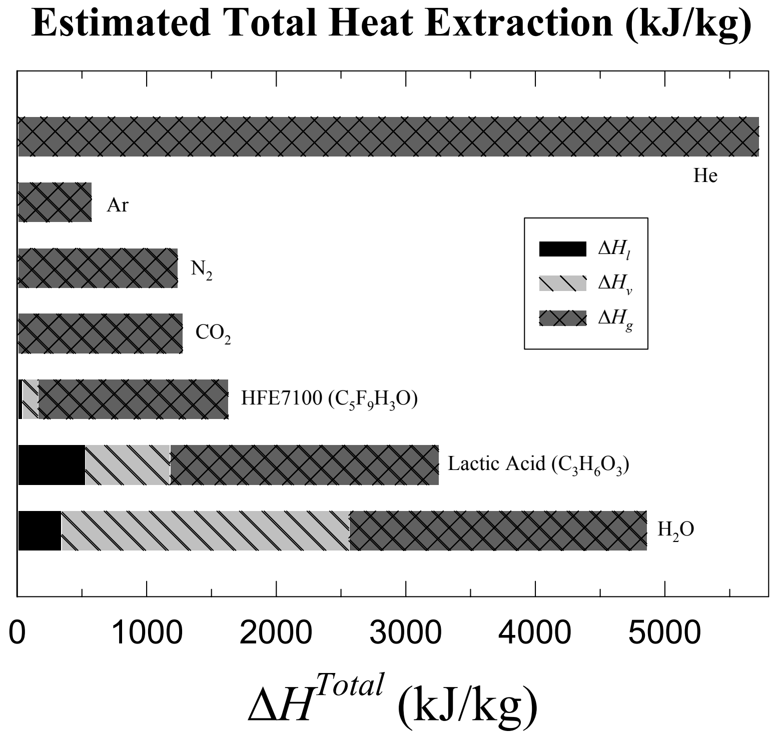


Figure 7–6. Relative Contributions of Liquid Heating, Vaporization, and Gas Heating to 1400 K to the Total Heat Absorbed by Various Thermal Agents.
(top: mole basis; bottom: mass basis)

Nitrogen and carbon dioxide were predicted to extract roughly the same amount of heat per kg, while the amount extracted by gaseous HFE-7100 was only slightly higher. In fact, it has been found that for a number of gaseous species expected to act primarily as thermal agents the mass required to extinguish a fire is roughly constant.[171] However, it is clear from these plots that this criterion should only be used to provide guidance and that it is not generally applicable to a wide range of molecular species.

The performance of HFE-7100 and lactic acid was evaluated using the Dispersed Liquid Agent Fire Suppression Screen (DLAFSS, Chapter 8). Despite lactic acid's expected ability to withdraw significant levels of heat from a flame zone, it is flammable. Thus, there will be competitive effects between the heat release and heat extraction in the suppression processes. To mitigate the effect of the heat release, lactic acid was mixed with water, also a good thermal agent, but nonflammable. Both the ether and the aqueous solution were introduced as droplets.

Figure 7–7 shows the test results for three lactic acid solutions. The undiluted stock solution was not tested because it was so viscous it caused the syringe pump, used to deliver the liquid to the nebulizer, to stall. Each data point represents an average of five or more tests; the error bars represent one standard deviation. The blow-off velocity decreased with increasing liquid application rate. In other words, as more of the acid mixture was delivered to the flame, less airflow was required to induce extinction.

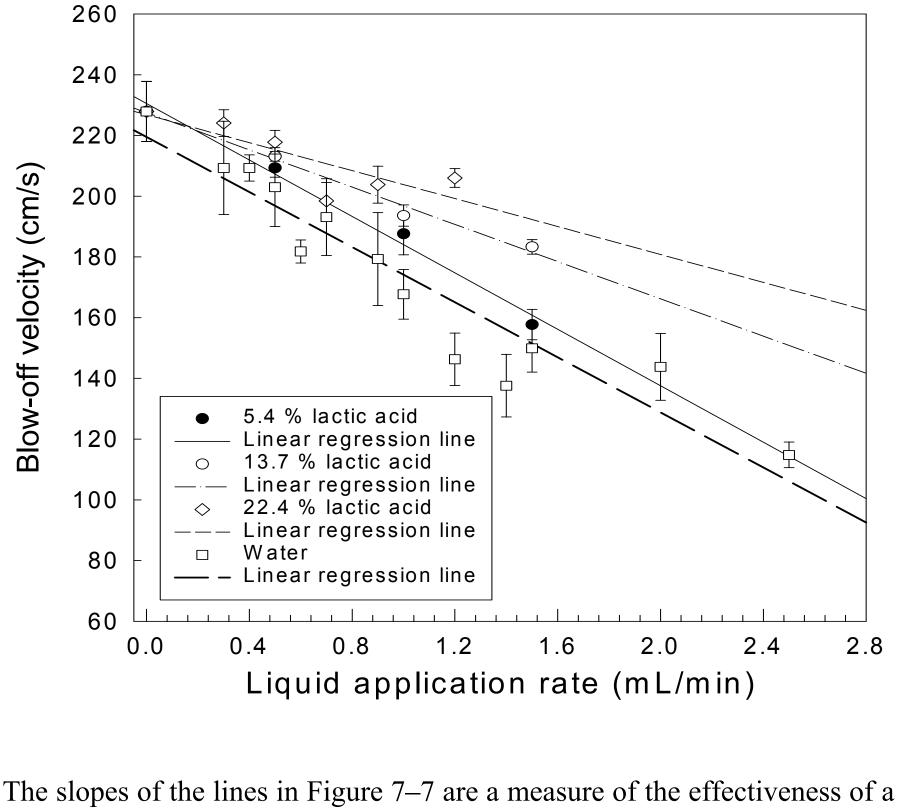


Figure 7–7. Air Velocities at Extinguishment of the DLAFSS Flame as a Function of Liquid Application Rate for Lactic Acid/water Mixtures.

The slopes of the lines in Figure 7–7 are a measure of the effectiveness of a liquid in suppressing a flame. The steeper the slope, the more effective is the liquid. The three lactic acid/water mixtures showed no improvement of fire suppression effectiveness over neat water. In fact, the fire suppression effectiveness decreased as the lactic acid mass fraction was increased. Given that no chemical effects were expected for fire suppression with lactic acid, it was concluded that the increased heat extraction due to lactic acid was being overwhelmed by heat release due to its combustion.

Figure 7–8 is a similar plot for HFE-7100. The shallower slope indicates a less efficient agent than water.

HFE-7100 was also studied in the Transient Application Recirculating Pool Fire (TARPF) facility (Chapter 8) to understand its performance under flow conditions typical of those present in aircraft engine nacelles. The airflow in the tunnel was fixed at 6.67 H 10^{-3} m^3/s. The porous burner was operated with a propane flow of 33 mL/s. The mist nozzle had a flow of 1.9 mL/s at 1.03 MPa. The mist discharge duration was varied from 1 s to 10 s. The hot surface used to investigate re-ignition was not activated. The only heating of this surface came from the impinging flame.

For these operating conditions, it was found that the pool fire stabilized behind the backward-facing step could not be completely suppressed by the HFE-7100 mist. Furthermore, the nominal effective mass fraction of the HFE-7100 for the TARPF experiments was more than twice as high as that required to extinguish a propane flame in the DLAFSS. A similar behavior was observed when water was tested. The difference is almost certainly associated with agent distribution and entrainment in the TARPF. It is likely that droplets of agent dispersed in the high-speed air flow had sufficient momentum to pass above the recirculating zone without being entrained. In this way, it would be possible to have an extinguishing concentration of liquid agent in the air above the flame, but a lower concentration in the actual location where the flame is stabilized. In either case, the results demonstrated the importance of agent distribution for effective flame extinguishment.

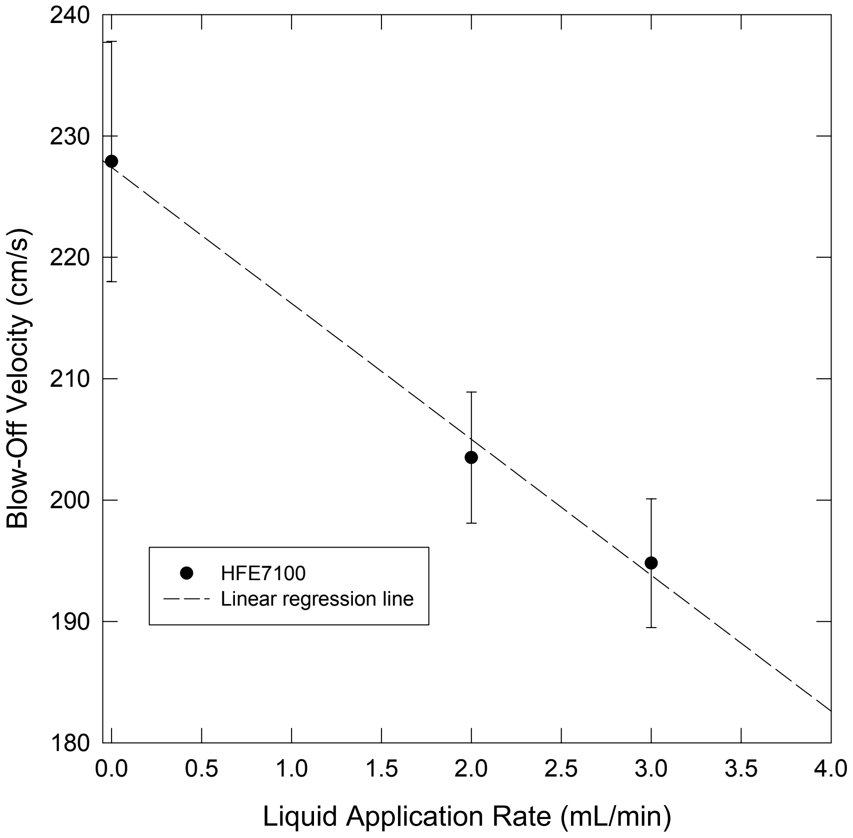


Figure 7–8. Air Velocities at Extinguishment of the DLAFSS Flame as a Function of Liquid Application Rate for HFE-7100.

Chemical Kinetic Modeling of Thermal Agents

To obtain further insights into the effectiveness of thermal agents and their mechanisms of flame extinguishment, detailed chemical-kinetic computations were performed in which various thermal agents were added to the air side of laminar opposed-flow diffusion flames.[147] The flames were simulated using OPPDIF,[172] a computer code developed by Sandia National Laboratories. OPPDIF is built on a number of general purpose subroutines, collectively known as CHEMKIN-III.[173] GRI-Mech 1.2, which had been developed with the support of the Gas Research Institute, provided the detailed kinetics for the methane/air flame.[174]

GRI-Mech 1.2 consisted of 32 chemical species undergoing 177 reactions. One- and two-carbon species were included. Thermodynamic and transport data were provided as separate files. The mechanism was created by starting with appropriate estimates for the rate constants and then optimizing to provide the best agreement with experimental measurements in such systems as premixed flames, shock tubes, and flow reactors.[174] The mechanism was not optimized using diffusion flame results. The extinction behavior for the propane/air flame was calculated using the mechanism of Babushok and Tsang.[175]

In the simulations, the goal was to identify the flow conditions just sufficient to cause extinction of a flame formed by fuel and either air or air with added agent. The approach was based on the hypothesis that the maximum flame temperature at extinguishment for a given fuel is a unique value as long as the agent is non-reactive in the flame. Most of the calculations were for methane/air flames, but some were performed for the computationally more intensive propane/air flames. An arbitrary, but stringent, criterion was adopted which defined the extinction velocity as that for which a burning solution was still obtained, but for which an increase of only 0.01 cm/s in the fuel and air initial velocities either resulted in (a) a failure to find a solution or (b) a non-burning solution. Additional small increases in velocity always resulted in non-burning solutions.

The general procedure was to find a solution for a given type of diffusion flame by first solving an isothermal case and using the solution as the input for a calculation in which the energy equation was added. Once that solution was available, it was used as the starting point for calculations in which such parameters as the oxidizer and flow velocities were changed. Only the formulation including the energy equation was solved for the "restarted" cases. The new solution then became the starting point for cases involving further changes in the controlling parameters. For a given set of initial conditions (fuel, agent fraction, etc.), higher and higher flow velocities were used until the above extinction criterion was met.

Checks against later GRI-Mech releases 2.11 and 3.0 showed no more than a minimal effect of the specific release on the calculated results.

Figure 7–9 shows the similarity of the calculated maximum flame temperatures at extinction, which were uniform at 1794 °C ± 7 °C. The three calculations of the strain rate of the flame at extinction were also close at 500 $s^{-1} \pm 6\ s^{-1}$. Other reported calculations show similar results, while reported experimental values from seven laboratories averaged 384 $s^{-1} \pm 21\ s^{-1}$.[147] Since all the calculations invoke similar chemistry, it is presumed that the difference between the (consistent) calculated values and the (consistent) measured values results from the particular chemical kinetic mechanism used. The uncertainties in the rate constants could readily account for the roughly 20 % difference.

For the propane/air flames, the calculated strain rate at extinction was 621 s^{-1}. The three reported values were 510 s^{-1}, 583 s^{-1}, and 721 s^{-1}.[147] This range of measured values is wider than that for the methane/air flames and encompasses the calculated value for the propane/air flame.

Table 7–24 lists the added volume fractions of inert gases calculated to extinguish a buoyancy dominated, methane/air diffusion flame. Previously published and NGP-measured values for each of the inert gases are included. Note that prior to the NGP, there was just one published value for flame extinguishment by the inert gases other than nitrogen. Details of all the measurements are included in Reference 147. Table 7−25 is a similar table for propane/air flames.

The following observations follow from the above data:

- For both fuels, the extinguishment values show some dependence on the type of burner.
- The calculated values agree with DLAFSS values, as expected since the extinguishing concentrations are tied to the experimental values for porous burners in opposed flow configurations.
- The helium results are consistently lower than the predicted values.
- Detailed chemical kinetic modeling, combined with the concept of a limit temperature, does a good job of capturing the relative effectiveness of thermal agents for extinguishing diffusion flames as well as the effects of using different fuels.

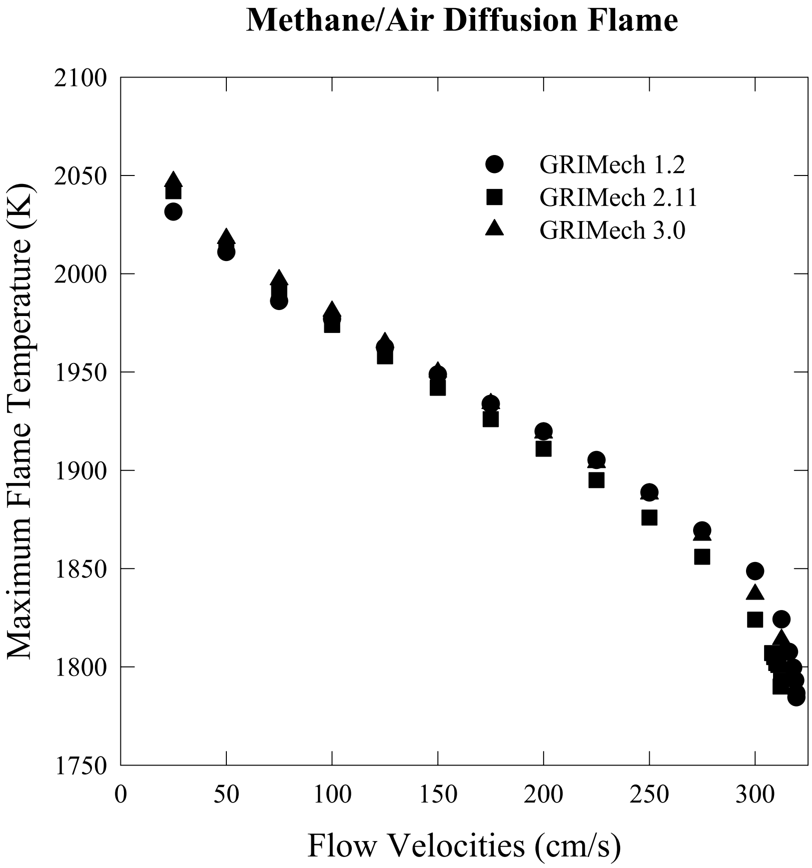


Figure 7–9. Maximum Flame Temperatures as a Function of the Equal Fuel and Air Velocity Magnitudes for a Methane/Air Opposed-Flow Diffusion Flame for Three Versions of the GRI-Mech Mechanism.

Table 7–24. Extinguishing Volume Fractions of Inert Gases for CH_4/Air Diffusion Flames.

Burner	N_2	Ar	He	CO_2	Reference
Calculated	0.33	0.43	0.33	0.22	147
Counterflow	0.34				179
Counterflow	0.32				176
Opposed Jet	0.29				177
Opposed Jet	0.30			0.19	178
Coflow	0.27				181
DLAFSS	0.33	0.47	0.21	0.24	147
Coflow	0.23	0.31	0.20	0.13	147

Table 7–25. Extinguishing Volume Fractions of Inert Gases for C_3H_8/Air Diffusion Flames.

Burner	N_2	Ar	He	CO_2	Reference
Calculated	0.39	0.50	0.39	0.28	147
Counterflow	0.39				179
Opposed Jet	0.35				177
Coflow	0.32				171
Coflow	0.33			0.20	180
Coflow	0.33				181
DLAFSS	0.26	0.55	0.22	0.26	147
Coflow	0.28	0.37	0.28	0.18	147

Chemical Kinetic Modeling of HFE-7100

In order to obtain some idea of the concentrations that might be required for extinguishment by a more general thermally acting agent, a series of calculations was carried out for HFE-7100. This calculation assumed that the only mechanism for heat extraction was the heat capacity of the gaseous agent, even though significant heat could also be removed by evaporation if the agent were released as a liquid at room temperature. This molecule was likely to decompose upon entering the high temperature region of the flame and then react to form final products. Reaction of the agent was not modeled. Due to the presence of a large number of fluorine atoms, it was also likely that the extinguishing efficiency would include a small chemical component.[182,183,184,185] On this basis, the result of this calculation was an upper limit for the required extinguishing concentration.

It is noteworthy that a relatively small volume fraction of $C_4F_9OCH_3$, 0.055, was required to lower the maximum flame temperature to the extinguishment temperature of 1550 K. The high heat capacity of this molecule, due to its large number of atoms, makes it a particularly effective thermal agent in molar terms. If liquid vaporization and chemical effects improved its effectiveness still further, this species might approach the effectiveness of halon 1301, which has an extinguishing volume fraction of 0.029 % on a molar basis.[186] On a mass basis, this fluorinated ether is less effective, based on the molecular weights of 148.9 g/mol for halon 1301 and 250 g/mol for $C_4F_9OCH_3$, but not dramatically so. It might be expected that the mass fraction of $C_4F_9OCH_3$ that must be added would be similar to other agents that do not have a strong component of chemical effectiveness.[171]

Two experimental measurements of the volume fractions of this compound required to extinguish diffusion flames have been identified. Unpublished measurements from the New Mexico Engineering Research Institute using a standard cup burner with heptane fuel yielded an extinguishing volume fraction of 0.061.[187] In a patent disclosure, Flynn and Scott also reported that a volume fraction of 0.061 was sufficient to extinguish a butane flame in a "micro-cup burner."[188] Given the limitations of the chemical kinetic simulation, there was reasonably good agreement.

At 300 K and atmospheric pressure, the saturation volume fraction of the ether in air was calculated to be 0.29. Thus, the saturation pressure at room temperature should be more than sufficient to extinguish a diffusion flame. Whether there would be time to establish this equilibrium would depend on the particular fire scenario. For example, in the event of an office building fire, there might well be time for sufficient evaporation to occur. Conversely, for an in-flight fire in an aircraft engine nacelle, the air flow through the nacelle would likely flush the agent faster than evaporation could establish an extinguishing concentration (Chapter 8).

Summary of Thermally Active Agents

There appear to be no gaseous chemicals that achieve a flame extinguishing efficiency comparable to halon 1301 purely through absorption of heat from flames. There may well be some liquid chemicals whose enthalpies of vaporization could augment the other thermal effects and achieve the desired efficiency.

HFC-7100 (methoxy-nonafluorobutane ($C_4F_9OCH_3$) appears to be the best of these liquid compounds. Its high boiling point suggests it would show promise as a streaming agent. Its equilibrium vapor pressure at room temperature is sufficiently high that it might be applicable for fires in enclosed spaces. As will be seen in Chapter 8, its high boiling point probably precludes its consideration for timely extinguishment of in-flight fires in cold engine nacelles and dry bays.

HFC-125 was a key reference compound due to its selection as the best commercially available agent under the TDP. On a mass basis, it is in an effectiveness class with the better non-aqueous thermal suppressants. Its boiling point, nearly as low as that of halon 1301, ensures superior low temperature dispersion. There is thus no clear reason to replace it with another compound that has no chemical fire suppression activity.

7.4.2 Tropodegradable Candidate Compounds

Atmospheric Chemistry and Tropodegradable Processes

The long atmospheric life of CF_3Br allows time for this chemical to travel from the earth's surface to the stratosphere where it is fragmented by ultraviolet radiation. The bromine atom then catalyzes ozone conversion to molecular oxygen. The initial reaction to the potency of the bromine catalysis was to search for replacement fire suppressants that were bromine-free.

Early in the 1990s, a halon replacement strategy emerged to reintroduce the chemical suppression effectiveness of bromine. This approach employed a "carrier molecular structure" with intrinsically very low atmospheric lifetime (on the order of days or weeks) to act as a carrier or base structure. To this, a bromine atom was added, resulting in a tropodegradable brominated fire extinguishant or tropodegradable bromocarbon. Since, in general, GWP and ODP values decrease with decreasing atmospheric lifetime, tropodegradable bromocarbons potentially solved the environmental problems (global warming and ozone depletion) while providing efficient fire suppression. Tropodegradable compound atmospheric lifetimes had in some cases been measured, but generally were estimated based on data generated for functional groups such as sites of unsaturation, numbers of C-H bonds, and substitution patterns. Early estimates of atmospheric lifetime for alkenes, which were as low as a few days, have since been demonstrated to be accurate.

The carrier compounds selected were generally partially fluorinated and incorporated chemical features that are reactive with atmospheric -OH or O_3, are photochemical reactive, or are inherently polar and therefore subject to atmospheric removal by the rainout process (Table 7–26).

Table 7–26. Tropodegradable Brominated Candidates.

Tropodegradable Base Structure	Corresponding Tropodegradable Bromocarbon
CF_3-O-CF_2H	CF_3-O-CF_2Br
CF_3-O-CFH_2	CF_3-O-CFBrH
CF_2H-O-CF_2H	CF_2H-O-CF_2Br
CH_2=$CHCF_3$	CH_2=$CBrCF_3$, CHBr=$CHCF_3$
CH_2=$CFCF_3$	CHBr=$CFCF_3$
CH_2=$CFCF_2H$	CH_2=$CHCF_2Br$, CHBr=$CFCF_2H$
CHF=$CHCF_3$	CFBr=$CHCF_3$, CHF=$CBrCF_3$

The reactions that cause atmospheric decomposition of' a molecule differ for alkenes, ethers, and amines, as summarized in Table 7–1. For alkenes, reaction with hydroxyl free radicals or with tropospheric or ground level ozone target the double bond, while ethers and amines are subject to hydrogen abstraction reactions by the -OH radical. Photolysis of the C-I bond is the predominant reaction pathway for iodinated fluoroalkanes such as CF_3I. Direct physical removal of alcohols through rainout is not contingent on the reactivity of the compound.

Compounds can also be degraded by reaction with a number of other atmospheric species, including oxygen atoms in the ^3P and ^1D electronic states, NO_x, nitric acid, and peroxy species. Such reactions are relatively minor tropospheric sinks for the chemicals considered here.[189]

A rate constant can be assigned to each of these processes: k_{OH} for reaction with hydroxyl free radicals, $k_{physical}$ for physical removal, k_{photo} for photolysis, and k_{O3} for reaction with tropospheric ozone. These rate constants vary not only with the chemical being removed from the troposphere, but are also a function of the atmospheric position (which determines the hydroxyl free radical concentration, temperature, and solar flux). As an approximation, one can use, for all but k_{photo}, the globally averaged rate constants. An overall pseudo first-order rate constant k_1 can be written, where $k_1 = k_{OH}[\bullet OH] + k_{physical} + k_{photo} + k_{O3}[O_3]$, $[\bullet OH]$ is a globally averaged tropospheric hydroxyl free radical concentration (9.7×10^5 cm^3/molec-s),[190] and $[O_3]$ is the globally averaged tropospheric ozone concentration (5.0×10^{11} cm^3/molec-s).[191]

Hydroxyl Free Radical Hydrogen Atom Abstraction

All compounds containing a hydrogen atom (e.g., hydrocarbons, HFCs, and HCFCs) are subject to reaction with tropospheric •OH. The organic free radical •R formed rapidly reacts with diatomic oxygen (O_2) to form a peroxy radical (ROO•), which further reacts to give a series of products. In most cases, these final products are rapidly removed by physical processes so that they do not contribute significantly to ozone depletion or global warming. For most saturated haloalkanes, this process is too inefficient to be considered as giving tropodegradable compounds.

For the compounds of interest here, a hydroxyl free radical can abstract a hydrogen atom and/or add to an unsaturated molecule to yield products (Reaction 7-33). The effectiveness of •OH reactions in removing compounds from the atmosphere depends on the reaction rate constant (k_{OH}) and the atmospheric concentration of •OH. The rate constant k_{OH} gives the time rate of change of the concentration of a compound C in the atmosphere due to reaction with •OH only (Equation 7-34) and can be written as the sum of the rate constants for hydrogen atom abstraction (k^1_{OH}) and for hydroxyl addition to an unsaturated compound (k^2_{OH}). The atmospheric half-life of a chemical for which the sole removal mechanism is reaction with •OH is given by Equation 7-35, which can be rewritten to yield the atmospheric lifetime (i.e., the e-folding lifetime), Equation 7-36.

$$\mathrm{C} + {\bullet}\mathrm{OH} \xrightarrow{k_{OH}} \text{products} \tag{7-33}$$

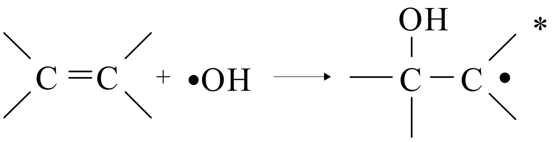
$$\frac{d[C]}{dt} = -k_{OH}[C][{\bullet}OH] \tag{7-34}$$

$$t_{1/2} = \frac{\ln 2}{k_{OH}[{\bullet}OH]} \tag{7-35}$$

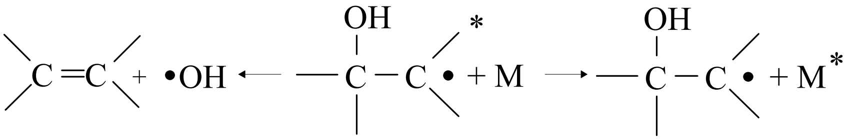
$$t_{1/e} = \frac{1}{k_{OH}[{\bullet}OH]} \tag{7-36}$$

Addition of •OH Free Radicals to Unsaturated Chemicals

Addition of •OH free radicals to unsaturated chemicals is a highly effective removal process. For alkenes, the •OH adds to give a highly energetic product radical (Reaction 7-37), where the asterisk indicates an activated species.). If it does not lose another group, the energetic product can then either revert back to reactants, or it can be stabilized by collision with another molecule (M), which can carry off the excess energy (Reaction 7-38). The reverse reaction is probably not important below 100 ºC, higher than temperatures found in the troposphere. Hydroxyl free radicals can also add to a triple bond (Reaction 7-39) and to aromatics. Due to potential manufacturing difficulties and stability problems, alkynes (compounds containing triple bonds) are not considered as halon replacement candidates; however, aromatic compounds are.



(7-37)



(7-38)

(7-39)

Photolysis

Photolysis (also called photodegradation and photolytic decomposition) requires absorption of electromagnetic radiation with resulting molecular decomposition. The photodecomposition reactions have the form shown in Reaction 7-40, where the products are fragments of the original reactant molecule. Planck's constant (h) multiplied by the frequency of the electromagnetic radiation (ν) gives the energy of a single photon of radiation with that frequency, and "$h\nu$" is often used as a symbol for a photon in a chemical equation (e.g., Reaction 7-40). As the frequency of the electromagnetic radiation increases and the wavelength (λ) decreases, the energy per photon increases. Thus, shorter wavelength electromagnetic radiation, such as ultraviolet (UV), is usually more effective in effecting photodegradation than is longer wavelength radiation, such as visible and infrared (IR). Photolysis of a molecule depends on two parameters, the absorption cross section (σ) (which determines how much of the available light is absorbed) and the quantum yield (φ) (the fraction of the absorbed photons that affects photolysis). If every photon absorbed produced a reaction, $\varphi = 1$.

$$\text{Reactant} + h\nu \rightarrow \text{Products} \qquad (7\text{-}40)$$

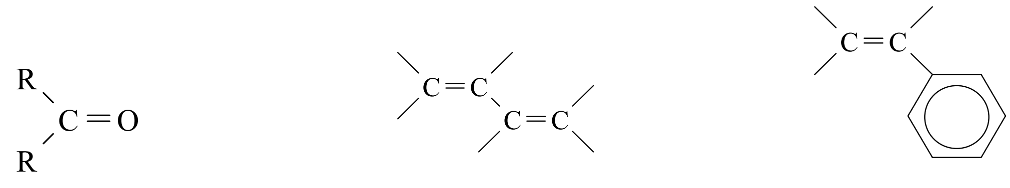
Most organic compounds exhibit decreasing absorption cross sections as the radiation wavelength increases (at least for the ultraviolet and visible spectral regions). Since much of the lower wavelength, higher energy solar radiation is removed by stratospheric ozone before sunlight reaches the troposphere (particularly UV-B radiation, with wavelengths between 180 nm and 320 nm many molecules do not encounter electromagnetic radiation of a sufficiently short wavelength for absorption until they reach the stratosphere. For example, the CFCs (chlorofluorocarbons) absorb little if any of the solar radiation required for photolytic decomposition as they pass through the troposphere. However, in the stratosphere, where short wavelength UV radiation is intense, the CFCs photodecompose to release chlorine atoms.

Photodissociation in the troposphere requires that a compound absorb radiation in the wavelength range from 299 nm to 700 nm. The photodissociation rate constant k_{photo} is determined by Equation 7-41, where $\sigma(\lambda)$ is the absorption cross section as a function of the wavelength, λ, $I(\lambda)$ is the solar intensity as a function of λ, and $\varphi(\lambda)$ is the photodissociation quantum yield. Thus, a chemical compound has two characteristics that determine the importance of photolysis: (1) the absorption cross section (how well it absorbs electromagnetic radiation encountered in the troposphere) and (2) the quantum yield. Both of these are a function of the electromagnetic radiation wavelength. The atmospheric lifetime for photodissociation only is then given by Equation 7-42.

$$k_{photo} = \int_{290\text{nm}}^{700\text{nm}} \sigma(\lambda) I(\lambda) \varphi(\lambda) d\lambda \qquad (7\text{-}41)$$

$$t_{1/e} = 1/k_{photo} \qquad (7\text{-}42)$$

In general, halocarbons require one of the groups shown in Figure 7–10 to be present for significant absorption and photodissociation in the troposphere (i.e., absorption for λ = 299 nm to 700 nm).



Carbonyl, R ≠ OH or OR | Conjugated Double Bonds | Double Bond Conjugated to Aromatic

-Br or -I

Polynuclear Aromatic | Nitro-Substituted Benzene | Bromine or Iodine

Figure 7–10. Groups Required for Significant Tropospheric Photodissociation.

Only the ketones and iodides were of major interest; however, compounds with conjugated double bonds (i.e., double bonds that allow some delocalization of the π electron cloud) and compounds containing a double bond conjugated to an aromatic could form the basis for more "exotic" fire suppressants, albeit with likely higher boiling points. In addition, photolysis of bromine compounds assists in lowering the atmospheric lifetimes for bromine-containing compounds (those proposed herein).

7.4.3 Bromofluoroalkenes

Criteria for Acquisition

The chemical family of bromofluoroalkenes represents an extensive array of structural possibilities. The examination began with an exhaustive listing and assessment of structural options, including structural isomers. Table 7–27 shows the range of variety just for C_3 compounds with 3, 4, or 5 fluorine atoms.

From the overall list, the following were concepts used to determine which compounds would be acquired for screening:

- Lowest boiling points in a given subgroup. Ideally, a compound's boiling point was published; some were estimated. The lowest boiling points were likely to be found among the more heavily fluorinated compounds (3, 4 or 5 atoms) and those with the fewest carbon atoms (2 or 3).

- Variation in chemical structure. This helped develop guidance for isomeric effects on flame extinguishment efficiency and volatility.
- Estimation of tendency to cause cardiac arrhythmia.
- Availability and cost from a commercial supplier or laboratory synthesis.
- Expected flame suppression efficiency. Since the bromine atom is always released in the flame zone, all the bromofluoroalkenes were expected to extinguish flames at 3 volume % to 4 volume %. This estimate was expected to be improved by increasing fluorination and decreasing hydrogenation. However, some fluoroalkenes were reported to be spontaneously flammable (e.g., CF_2=CFBr[192]), complicating selection and prediction of effectiveness.

Table 7–27 Bromofluoropropenes.

Chemical Name	Chemical Formula	cis/trans Isomers
2-bromo-1,1,3,3,3-pentafluoropropene	$CF_2=CBrCF_3$	
3-bromo-1,1,2,3,3-pentafluoropropene	$CF_2=CFCF_2Br$	
1-bromo-1,2,3,3,3-pentafluoropropene	$CFBr=CFCF_3$	Y
3-bromo-1,1,3,3-tetrafluoropropene	$CF_2=CHCF_2Br$	
2-bromo-1,3,3,3-tetrafluoropropene	$CFH=CBrCF_3$	Y
1-bromo-1,2,3,3-tetrafluoropropene	$CFBr=CFCF_2H$	Y
1-bromo-1,3,3,3-tetrafluoropropene	$CFBr=CHCF_3$	Y
3-bromo-1,2,3,3-tetrafluoropropene	$CHF=CFCF_2Br$	Y
3-bromo-1,1,2,3-tetrafluoropropene	$CF_2=CFCFHBr$	
2-bromo-1,1,3,3-tetrafluoropropene	$CF_2=CBrCF_2H$	
2-bromo-3,3,3-trifluoropropene	$CH_2=CBrCF_3$	
3-bromo-1,3,3-trifluoropropene	$CFH=CHCBrF_2$	Y
2-bromo-3,3,3-trifluoropropene	$CHBr=CHCF_3$	Y
2-bromo-1,1,3-trifluoropropene	$CF_2=CBrCFH_2$	
2-bromo-1,3,3-trifluoropropene	$CFH=CBrCF_2H$	Y
3-bromo-1,1,2-trifluoropropene	$CF_2=CFCBrH_2$	
3-bromo-1,2,3-trifluoropropene	$CFH=CFCFBrH$	Y
3-bromo-1,1,3-trifluoropropene	$CF_2=CHCFBrH$	
3-bromo-2,3,3-trifluoropropene	$CH_2=CFCF_2Br$	
1-bromo-2,3,3-trifluoropropene	$CHBr=CFCHF_2$	Y
1-bromo-1,2,3-trifluoropropene	$CFBr=CFCFH_2$	Y
1-bromo-1,3,3-trifluoropropene	$CBrF=CHCHF_2$	Y
1-bromo-2,3,3,3-tetrafluoroproprene	$CHBr=CFCF_3$	Y

It was presumed that the atmospheric lifetimes would be short. In the case of the halogenated propenes, atmospheric lifetimes are limited primarily by atmospheric OH radical reactions and estimated to be on the order of a week. For example, 2-bromo-3,3,3-trifluoropropene was estimated to have an atmospheric lifetimes of 4 days.[193]

Cup Burner Extinguishment

Several of these compounds were acquired in small (5 g) quantities and their cup burner extinguishment evaluated. As the first of the tropodegradable families examined, two groups were investigated.

Table 7–28 includes chemicals with a range of carbon content (3 atoms to 5 atoms) and structural variation, and three or more fluorine atoms. While these differences had significant impact on the boiling points, there was essentially no effect on the concentration needed to extinguish a cup burner flame.[194,195,196] The values were as expected and acceptable, given the presence of a bromine atom and some hydrogen fuel in each molecule.

The second group involved the most volatile compounds. Flammability, air reactivity, or markedly higher cup burner extinguishment values in the fluorinated ethenes eliminated further consideration of these lowest boiling alkenes. Table 7–29 shows the cup burner values and boiling points of the most volatile propenes (and one ethene). None of the substituted propenes met the volatility criterion. There was no effect of structure on the extinguishing concentrations.

Table 7–28 Bromofluoropropene Cup Burner Flame Extinguishment Data.

Compound Name	Chemical Formula	T_b (°C)	Vol. %
1-Bromo-3,3,3-trifluoropropene	$CF_3CH=CHBr$	40	3.5 [a]
3-Bromo-3,3-difluoropropene	$CBrF_2CH=CH_2$	42	4.5
2-Bromo-3,3,3-trifluoropropene	$CF_3CBr=CH_2$	34	2.6
4-Bromo-3,3,4,4-tetrafluorobutene	$CF_2BrCF_2CH=CH_2$	54	3.5
2-Bromo-3,3,4,4,4-pentafluorobutene	$CF_3CF_2CBr=CH_2$	56	3.8 [a]
2-Bromo-3-trifluoromethyl-3,4,4,4-tetrafluorobutene	$CF_3C(CF_3)FCBr=CH_2$	78	3.3 [a]
1-Bromo-2-trifluoromethyl-3,3,3-trifluoropropene	$(CF_3)_2C=CHBr$	63	2.6 [a]
1-Bromo-4,4,4,3,3-pentafluorobutene	$CF_3CF_2CH=CHBr$	58	3.1 [a]
2-Bromo-3,3,4,4,5,5,5-heptafluoropentene	$CF_3CF_2CF_2CBr=CH_2$	78	3.7 [a]
2-Bromo-3- trifluoromethoxy)-3,4,4,4-tetrafluorobutene	$CF_3CF(CF_3O)CBr=CH_2$	75	3.8 [a]

a Testing performed using premixed agent/air mixtures

Table 7–29 Low Boiling Bromofluoroalkene Cup Burner Values.

Compound Name	T_b (°C)	Volume %
1-Bromo-pentafluoropropene	27	3.1
2-Bromo-pentafluoropropene	25	3.5
3-Bromo-1,1,3,3-tetrafluoropropene	33	3.3
2-Bromo-1,3,3,3-tetrafluoropropene	29	3.5
2-Bromo-1,1,3,3-tetrafluoropropene	29	3.3
1-Bromo-2,3,3,3-tetrafluoropropene	30 (est.)	3.3
2-Bromo-3,3,3-trifluoropropene	32-34	3.1
1-Bromo-1,2-difluoroethene	20 to 24 (est.)	8.4

The cup burner extinguishment performance of the substituted ethene was outside the range for continued consideration. The isomeric compound (1-bromo-2,2-difluoroethene, $CHBr=CF_2$) is flammable. This demonstrated the potential for strong effects of structural isomerism on flammability in these very small molecules. While 1-bromo-1,2-difluoroethene serves as a bromine carrier, this was clearly not sufficient to assure an acceptable cup burner value.

In summary, there are trifluorinated, tetrafluorinated and pentafluorinated bromopropenes that all are good extinguishants with no indications of flammability. However, bromofluoropropene boiling points lower than 25 °C are extremely unlikely. If the low temperature limit were raised, these compounds could prove useful in aircraft applications, subject to atmospheric lifetime and toxicity testing.

7.4.4 Fluoroalkoxide and Fluoroalkyl Phosphorus Compounds

Criteria for Acquisition

The approach to compound selection was similar to that for the bromocarbons in Section 7.4.3. However, there were multiple toxic effects, rather than a focus on cardiac arrhythmia. The substitution of F atoms for H atoms was expected to lower the boiling point and increase flame suppression efficiency. Syntheses for many of the compounds were complex or untried, and this was a limiting factor in the research.

Toxicity

There is a large amount of toxicity data available for phosphorus compounds. In part, this is because a number of phosphorus compounds (particularly phosphite esters) are cholinesterase inhibitors. The toxicity of phosphorus compounds is highly variable. Thus, toxicity must be given careful consideration. There is limited information indicating that toxicity may increase from phosphates to phosphites to phosphines. Phosphonitriles appear to have relatively low toxicities, but some show indications of mutagenicity. The presence of P-halogen bonds can cause severe irritation and lung damage owing to hydrolysis with formation of phosphorus-containing and hydrohalic acids. For this reason, compounds containing direct halogen atom bonds to phosphorus atoms are poor candidates as halon substitutes.

Table 7–30 contains information on the toxicity and safety of some phosphorus-containing chemicals related to compounds of interest here.

Table 7–30 Phosphorus Compound Toxicity (Safety) Information.

Compound Name	Formula	CAS No.	Observations [a]
Bis(trifluoromethyl)-chlorophosphine	$PCl(CF_3)_2$	650-52-2	[BLO280] Ignites spontaneously in air. HR = 3.
Dibutylphosphate	$O=P(OH)(OC_4H_9)_2$	107-66-4	{RTECS HS630000} [DEG600] LD_{50} (rat, oral) = 3200 mg/kg. Moderately toxic by ingestion. HR = 2.
Dibutylphosphonate	$O=PH(OC_4H_9)_2$	1809-19-4	{RTECS HS6475000} [DEG800] LD_{50} (rat, oral) = 3200 mg/kg, LD_{50} (rabbit, skin) = 1990 mg/kg. Moderately toxic by ingestion, skin contact. Severe eye irritant. HR = 2.
Diethylphosphonate	$O=PH(OC_2H_5)_2$	762-04-5	{RTECS TG7875000} [DJW400] LD_{50} (rat, oral) = 3900 mg/kg, LD_{50} (rabbit, skin) = 2165 mg/kg. Moderately toxic by ingestion, skin contact. HR = 2.

Compound Name	Formula	CAS No.	Observations [a]
Diisopropyl methylphosphonate	$O{=}P(CH_3){-}[OCH(CH_3)_2]_2$	1445-75-6	{RTECS SZ9090000} [DNQ875] LD$_{50}$ (rat, oral) = 826 mg/kg, LD$_{50}$ (mouse, oral) = 1041 mg/kg. Moderately toxic by ingestion, skin contact. HR = 2.
Diisopropylphosphonate	$O{=}PH[OCH(CH_3)_2]_2$	1809-20-7	{RTECS SZ7660000} [DNQ600] LD$_{50}$ (rat, oral) = 3100 mg/kg, LD$_{50}$ (rabbit, skin) = 5700 mg/kg. Moderately toxic by ingestion. Mildly toxic by skin contact. HR = 2.
Dimethyl(1,2-dibromo-2,2-dichloroethyl) phosphate	$O{=}P(OCH_3)_2{-}(OCHBrCBrCl_2)$	300-76-5	{RTECS TB9540000} [DRJ600] LD$_{50}$ (rat, inh) = 7700 µg/kg, LD$_{50}$ (mouse, inh) = 156 mg/kg, LD$_{50}$ (rat, oral) = 250 mg/kg, LD$_{50}$ (rabbit, skin) = 1100 mg/kg. Poison by ingestion, inhalation. Moderately toxic by skin contact. Skin irritant. Insecticide of the cholinesterase inhibitor type. HR = 3.
Dimethyl(2,2-dichloroethenyl)-phosphate	$O{=}P(OCH_3)_2{-}(CH{=}Cl_2)$	62-73-7	{RTECS TC0350000} [DRK200] LC$_{50}$ (rat, inh, 4 hr) = 15 mg/m3, LC$_{50}$ (mouse, inh, 4 hr) = 13 mg/kg, LD$_{50}$ (rat, oral) = 25 mg/kg, LD$_{50}$ (rabbit, skin) = 107 mg/kg. Poison by ingestion, inhalation, skin contact, intraperitoneal, intravenous, subcutaneous. Experimental teratogen, suspected carcinogen Cholinesterase inhibitor. HR = 3.
Dimethylphosphonate	$O{=}PH(OCH_3)_2$	868-85-9	{RTECS SZ7710000} [DSG600] LD$_{50}$ (rat, oral) = 3050 mg/kg, LD$_{50}$ (rabbit, skin) = 2400 mg/kg. Moderately toxic by ingestion, skin contact. Experimental carcinogen. Skin, eye irritant. HR = 3.
Hexaethyltetraphosphate	$OP(OC_2H_5)_2{-}[OP(O)(OC_2H_5)]_2{-}OP(O)(OC_2H_5)_2$	757-58-4	{RTECS XF1575000} [HCY000] LD$_{50}$ (rat, oral) = 7 mg/kg, LD$_{50}$ (mouse, oral) = 56 mg/kg, LD$_{LO}$ (rat, skin) = 15 mg/kg. Poison by ingestion, skin contact, intraperitoneal, subcutaneous, intravenous, intramuscular. HR = 3.
Tris(2-chloroethyl) phosphite	$O{=}P(OCH_2CH_2Cl)_2{-}(CH_2CH_2Cl)$ [b]	140-08-9	{RTECS KK2810000} [PHO000] LD$_{50}$ (rat, oral) = 100 mg/kg, LD$_{50}$ (rabbit, skin) = 810 mg/kg. Poison by ingestion, intraperitoneal. Moderately toxic by skin contact. Severe eye irritant. HR = 3.

Compound Name	Formula	CAS No.	Observations [a]
Tris(2-fluoroethyl) phosphite	$O=P(OCH_2CH_2F)_2$-(CH_2CH_2F) [b]	63980-61-0	{RTECS KL1925000} [PHO250] LC_{LO} (rat, inh, 10 min) = 500 mg/m3, LC_{LO} (mouse, inh, 10 min) = 1000 mg/m3. Poison by inhalation. HR = 3.
Triethylphosphite	$O=P(C_2H_5)(OC_2H_5)_2$ [b]	122-52-1	{RTECS TH1130000} [TJT800] LD_{50} (rat, oral) = 3200 mg/kg. Moderately toxic by ingestion. Skin, eye irritant. HR = 2.
Tris(1-bromo-3-chloroisopropyl)-phosphate	$O=P[OCBr$-$(CH_3)(CH_2Cl)]_3$	7328-28-1	{RTECS TC8600000} [TNE500] Mutagenic data. HR = D (insufficient data).
Triisooctylphosphite	$O=P[(CH_2)_5CH$-$(CH_3)_2]$-$[O(CH_2)_5CH(CH_3)_2]_2$ [b]	25103-12-3	{RTECS TH1150000} [TKT000] LD_{50} (rat, oral) = 9200 mg/kg, LD_{50} (rabbit, skin) = 3970 mg/kg. Moderately toxic by skin contact. Mildly toxic by ingestion. Skin irritant. HR = 2.
Triisopropylphosphite	$O=P[CH(CH_3)_2]$-$[OCH(CH_3)_2]_2$ [b]	116-17-0	{RTECS TH2800000} [TKT500] LD_{50} (rat, oral) = 167 mg/kg. Poison by ingestion. Moderately toxic by intraperitoneal. HR = 3.
Trimethylphosphite	$O=P(CH_3)(OCH_3)_2$b	121-45-9	{RTECS TH1400000} [TMD500] LD_{50} (rat, oral) = 1600 mg/kg, LD_{LO} (rabbit, skin) = 2200 mg/kg. Moderately toxic by ingestion, skin contact. Experimental teratogen. Severe skin, eye irritant. HR = 2.
Tributylphosphine oxide	$O=P(C_4H_9)_3$	814-29-9	{RTECS SZ1575000} [TNE750] Poison by intravenous route. Eye irritant. HR = 3.
Tritolylphosphate (tricresylphosphate)	$O=P(OC_6H_5CH_3)_3$	1330-78-5	{RTECS TD0175000} [TNP500] LD_{50} (rat, oral) = 5190 mg/kg, LD_{50} (mouse, oral) = 3900 mg/kg. Poison by ingestion. Moderately toxic by skin contact. Eye, skin irritant. HR = 3.
Tri-2-tolylphosphate (tri-o-cresylphosphate)	$O=P(OC_6H_5CH_3)_3$	78-30-8	{RTECS TD0350000} [TNP750] LD_{50} (rat, oral) = 1160 mg/kg. Poison by ingestion, subcutaneous, intramuscular, intravenous, intraperitoneal. Moderately toxic by ingestion. HR = 3.
Dimethylfluorophosphate	$C_4H_{10}FO_3P$	358-74-7	{RTECS TE5600000} [DJJ400] LC_{50} (rat, inh, 10 min) = 7 g/m3, LC_{50} (mouse, inh, 10 min) = 500 mg/m3. Poison by inhalation, skin. HR = 3.

Compound Name	Formula	CAS No.	Observations [a]
Dimethylfluorophosphate	$C_2H_6FO_3P$	5954-50-7	{RTECS TE6125000} [DSA800] LC_{50} (rat, inh, 1 min) = 1800 mg/m3, LC_{50} (mouse, inh, 10 min) = 290 mg/m3. Poison by inhalation, skin contact, intravenous. HR = 3.
2-Ethyl-2(hydroxymethyl)-1,3-propane-diol, cyclic phosphate (1:1)	$C_6H_{11}O_4P$	1005-83-2	{RTECS TX6475000} [ELJ500] LC_{50} (rat, inh, 1 hr) = 30 mg/m3. Poison by ingestion, inhalation, skin contact, intraperitoneal and intravenous routes. HR = 3.
Ethyl isopropyl fluorophosphonate	$C_5H_{12}FOP$	None assigned	{RTECS SZ8552000} [ELX100] LC_{50} (rat, inh, 10 min) = 260 mg/m3, LC_{50} (mouse, inh, 5 min) = 245 mg/m3. Poisonous by inhalation, skin contact, and subcutaneous routes. HR = 3.
Hexamethyl phosphoramide	$C_6H_{18}N_3OP$	680-31-9	{RTECS TD0875000} [HEK000] TC_{LO} (rat, inh, 52 wk continuous) = 50 ppb, carcinogenic. An experimental carcinogen and tumorigen. Moderately poisonous by ingestion, skin contact, intraperitoneal, intravenous. Experimental reproductive effects. Human mutagenic data. HR = 3.
Triphenylphosphite	$O=P(C_6H_5)(OC_6H_5)2^b$	101-02-0	{RTECS TH1575000} [TMU250] LD_{50} (rat, oral) = 1600 mg/kg, LD_{50} (mouse, oral) = 1333 mg/kg. Poison by intraperitoneal, subcutaneous. Moderately toxic by ingestion. Severe skin irritant. HR = 3.
Tris(2-bromoethyl) phosphate	$O=P(OCH_2CH_2Br)]_3$	27568-90-7	{RTECS TC8480000} [TNE600] LC_{LO} (rat, inh) = 260 mg/m3. Poison by inhalation. Mutagenic data. HR = 3.
Isopropyl methyl fluorophosphonate	$C_4H_{10}FO_2P$	107-44-8	{RTECS TA8400000} [IPX000] LD_{50} (rat, inh, 10 min) = 150 mg/m3, LD_{50} (mouse, inh, 30 min) = 5 mg/m3, TC_{LO} (man, inh) = 90 µg/m3 (eyes), LC_{50} (human, inh) = 70 mg/m3. Deadly human poison by skin contact and inhalation. HR = 3.
Mevinphos (2-carbomethoxy-1-methylvinyl dimethyl phosphate)	$C_7H_{13}O_6P$	7786-34-7	{RTECS GQ5250000} [MQR750] LC_{50} (rat, inh, 1 hr) = 14 ppm. Poison by ingestion, inh, skin contact, subcutaneous, intravenous, intraperitoneal. HR = 3.

Compound Name	Formula	CAS No.	Observations [a]
Monocrotophos (3-hydroxy-N-methyl-cis-crotonamide, dimethyl phosphate)	$C_7H_{14}NO_5P$	6923-22-4	{RTECS TC4375000} [MRH209] LC_{50} (rat, inh, 4 hr) = 63 mg/m3. Poison by ingestion, inh, skin contact, intraperitoneal, subcutaneous, and intravenous routes. Mutagenetic data. HR = 3.
Tetraethylpyrophosphate	$P(O)(OC_2H_5)_2$-$OP(O)(OC_2H_5)_2$	107-49-3	{RTECS UX6825000} [TCF250] LD_{50} (rat, oral) = 500 µg/kg, LD_{50} (mouse, oral) = 7 mg/kg, LD50 (rat, skin) = 2400 µg/kg. Poison by ingestion, skin contact, intraperitoneal, intramuscular, other. Cholinesterase inhibitor. HR = 3.
Triethylphosphate	$O{=}P(OC_2H_5)_3$	78-40-0	{RTECS TC7900000} [TJT750] LD_{LO} (rat, oral) = 1600 mg/kg, LD_{LO} (mouse, oral) = 1600 mg/kg. Moderately toxic by ingestion, intraperitoneal, and intravenous. Reproductive effects. Mutagenic data. Cholinesterase inhibitor. HR = 2.
1,1,1-Trishydroxy-methylpropane bicyclic phosphite	$C_6H_{11}O_3P$	824-11-3	{RTECS TY6650000} [TNI750] LC_{LO} (rat, inh, 4 hr) = 10 ppm. A poison by ingestion, inhalation, skin contact, intraperitoneal, and intravenous routes. HR = 3.

[a] The SAX No. (Reference 67) is given in brackets followed by information from that reference; the RTECS No. (Reference 138) is given in braces. "HR" denotes the SAX Hazard Rating.

[b] The most probable (phosphonate) structure is given for these compounds, which can also be assigned the phosphite structure ($P(OR)_3$). Both forms may exist.

Flame Chemistry and Flammability

A description of the inhibition chemistry of phosphorus appeared in Chapter 3, and Section 7.3.5 of this chapter described the behavior of largely inorganic phosphorus-containing compounds. Over 40 years ago, it was proposed that the flame extinguishment action of $POCl_3$ was due to the chlorine and that its high efficiency was due to ready formation of HCl in the flame.[197] Subsequent research found that $POCl_3$ was about 10 times more effective than an equivalent amount of chlorine.[198]

Liquid halocarbons containing both phosphates and phosphites had been claimed as fire extinguishants.[199] Phosphates and phosphate esters had been of particular interest as fire suppressants since they are difficult to ignite and self-extinguish.[200] Trimethylphosphate ($(O{=}P(OCH_3)_3)$) showed a more pronounced effect on flame velocity than Cl_2 or Br_2.[201] In an opposed-jet burner, dimethylmethylphosphonate (DMMP, $O{=}P(CH_3)(OCH_3)_2$) was about 4 times more effective than halon 1301.[202] However, studies on flat $H_2/O_2/Ar$ flames indicated that DMMP acted as a flame promoter.[203] No cup burner values have been determined for DMMP, and it would be difficult to obtain such values because of its very high boiling point (181 °C [58]) and low vapor pressure (160 Pa at 25 °C [204]).

The estimated extinguishment concentrations of a broad range of organophosphates and phosphonates were estimated using a screening method based on the Flame Ionization Detector (FID) response of each compound (Table 7–31).[205,206,ii] The data presented in Table 7–31 indicate that in general the non-fluorinated phosphates and phosphonates may well be efficient extinguishants. However, many of the compounds are flammable, and they all have high boiling points.

Table 7–31. FID Extinguishment Estimates of Phosphorus Acids and Esters.

Compound Name	Structure	FID Extinguish. (volume %)
Trimethyl phosphate	$O=P(OCH_3)_3$	0.6 – 2.8
Dimethyl methylphosphonate	$O=P(OCH_3)_2CH_3$	0.7
Diethyl methylphosphonate	$O=P(OC_2H_5)CH_3$	0.9
Dimethyltrifluoroethyl phosphate	$O=P(OCH_3)_2OCH_2CF_3$	0.7
Diethyltrifluoroethyl phosphate	$O=P(OC_2H_5)_2OCH_2CF_3$	0.7
Diethylpentafluoropropyl phosphate	$O=P(OC_2H_5)_2OCH_2CF_2CF_3$	0.7
Diethylhexafluoroisopropyl phosphate	$O=P(OC_2H_5)_2OCH(CF_3)_2$	0.7
Diethylheptafluorobutyl phosphate	$O=P(OC_2H_5)_2OCH_2CF_2CF_2CF_3$	0.6
Diethyloctafluoropentyl phosphate	$O=P(OCH_2H_5)_2OCH_2CF_2CF_2CFCF_2H$	1.1
Bis(2,2,2-trifluoroethyl)-2.2,3.3,3-pentafluoropropyl phosphate	$O=P(OCH_2CF_3)_2OCH_2CF_2CF_3$	0.7
Tris(2,2,2-trifluoroethyI) phosphate	$O=P(OCH_2CF_3)_3$	0.8
Tris(2,2,3.3,3-pentafluoro-l-propyl) phosphate	$O=P(OCH_2CF_2CF_3)_3$	1.0
Tris(2,2,3,3,4,4,4-heptafluoro-l-butyl) phosphonate	$O=P(OCH_2CF_2CF_2CF_3)_3$	1.8

Laboratory studies had also found that decomposition of organophosphorus compounds could generate additional fuel. Gas phase studies in nitrogen found that diethylmethylphosphonate (DEMP, $O=P(CH_3)(OCH_2CH_3)_2$) pyrolyzed to form ethene ($CH_2=CH_2$), ethanol (CH_3CH_2OH), and ethylmethylphosphonate ($O=P(OH)(CH_3)(OCH_2CH_3)$).[207] Formation of ethene may have resulted from formation of a six-membered ring transition state or by scission of a PO-CH_2CH_3 bond with subsequent loss of a hydrogen atom from the ethyl radical (•CH_2CH_3). Similar results have been found in pyrolysis studies of diisopropylmethylphosphonate (DIMP), which generated propene ($CH_2=CHCH_3$), 2-propanol ($CH_3CH(OH)CH_3$), isopropylmethylphosphonate (IMP, $O=P(OH)(CH_3)(OCH(CH_3)_2)$), and methylphosphonic acid (MPA, $O=P(OH)_2(CH_3)$).[208] A six-membered ring transition state (Figure 7–11) was proposed for formation of 2-propene. Derivatization followed by gas chromatography-mass spectrometry has identified DMP, (dimethylphosphate ($O=P(OH)(OCH_3)_2$), monomethylphosphate ($O=P(OH)_2(OCH_3)$), MPA, orthophosphoric acid ($O=P(OH)_3$), phosphorous acid ($P(OCH_3)_3$), and phosphonic acid ($O=PH(OH)_2$) as combustion products in a $CH_4/O_2/N_2$ flame doped with DMMP.[209]

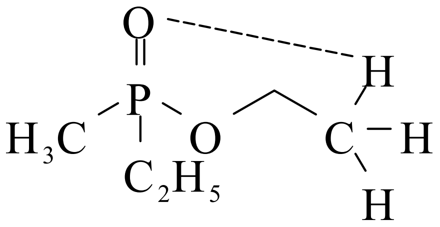


Figure 7–11. Formation of a Six-membered Ring Transition State.

[ii] The FID extinguishment values are quite different from those obtained using a cup burner. This is because the gas chromatograph FID technique enables estimation of relative extinguishment performance for a small hydrogen flame. This is not equivalent to the extinguishment of a heptane pool.

Attempts to determine a cup burner extinguishment value for a high volatility, nonfluorinated compound, trimethylphosphite ($P(OCH_3)_3$) have also been unsuccessful, due to its flammability. Each of the phosphorus compounds discussed above is, in fact, flammable at some concentration.

Nonetheless, there was good reason to expect efficient flame suppression from a phosphorus-containing compound (PCC), as long as (a) it decomposed to release the phosphorus atom and (b) the flammability was mitigated. This expectation led to extensive NGP examination of a range of families of PCCs in which a significant portion of the molecule was organic.

There are two ways around the flammability problem. One is to blend the material with a nonflammable carrier; the other is to work with fluorinated alkyl derivatives of phosphorus. The NGP examined both of these approaches using the cup burner.

Preliminary Fluoroalkoxide Phosphorus Flame Suppression Testing

Examination of prior studies and materials properties indicated that alkylphosphonitriles were not ideal for testing owing to their low volatility, and that phosphines were likely too toxic to consider, except possibly for mechanistic studies. Table 7–32 presents seven available phosphorus-containing compounds selected for preliminary testing, along with key properties.

Table 7–32 Properties of Phosphorus-Containing Compounds.

Compound Name	Formula	T_b, °C (kPa)	Flash Point, °C
Dimethylmethylphosphonate	$O{=}P(CH_3)(OCH_3)_2$	181 (101)[210]	68 [210]
Trimethylphosphate	$O{=}P(OCH_3)_3$	197 (101)	None
Trimethylphosphite	$P(OCH_3)_3$	111-112 (101)	27
(Bromodifluoromethyl) diethylphosphonate	$O{=}P(CBrF_2)(C_2H_5)_2$	99-102 (2.1)[211] 220 (101)[a]	Not available
Hexamethylphosphoramide	$O{=}P(N(CH_3)_2)_3$	230-232 (98)	Not available
Bis(2,2,2-trifluoroethyl)phosphite	$O{=}PH(OCH_2CF_3)_2$	43-44 (0.26)[210] 190 (101)[210]	76 [210]
Tris(2,2,2-trifluoroethyl)phosphite	$P(OCH_2CF_3)_3$	130-131 (99)[210]	>110[210]

a Estimated using pressure-temperature nomograph.

Testing of dimethylmethylphosphonate ($O{=}P(CH_3)(OCH_3)_2$) was attempted using the Standard NMERI cup burner but due to its high boiling point, the material was difficult to volatilize. The elevated temperature caused some decomposition to a black, tarry substance. A single test gave an extinguishing value of 5 volume %. This was considered a maximum value because not all the compound was available to extinguish the fire.

Trimethylphosphate ($O{=}P(OCH_3)_3$) was also difficult to test due to its high boiling point. The extinguishment value of 6.6 volume % is high, as it was observed that a small amount of the compound did not volatilize in the mixing chamber. With a higher chamber temperature (328 °C), an extinguishment value of 6.8 volume % was obtained; however, again, some of the compound in the mixing chamber did not volatilize. At a mixing chamber temperature of 344 °C, a cup burner value of 5.3 volume % was obtained. This value was also suspect, since the n-heptane in the fuel cup boiled and was difficult to control.

Trimethylphosphite ($O{=}P(OCH_3)_3$) was flammable and ignited. Complete extinguishment of the n-heptane flame was not achieved.

Only a small amount of (bromodifluoromethyl)diethylphosphonate ($O{=}P(CBrF_2)\text{-}(C_2H_5)_2$) was available. During the first test, the flame extinguished readily at a value of 4.7 volume %. The second test employed approximately one-third that of the first test. Even though the temperature of the heated chamber at the base of the cup burner was 250 °C, it appeared that the compound did not volatilize completely. The flame continued to show some extinguishment from the compound after the syringe pump was turned off, which indicated that the compound in the mixing chamber continued to volatilize even after the agent supply was stopped. The temperature of the heated chamber was therefore increased to 300 °C and the compound appeared to volatilize, but n-heptane boiling was observed at the extinguishment point of 1.4 volume %. Thus, the extinguishment concentration was estimated to be between 1.4 volume % and 4.7 volume %. A test with an increased flow and a slightly lower chamber temperature (270 °C) resulted in an extinguishment value of 3.3 volume %.

Testing of hexamethylphosphoramide ($O{=}P[N(CH_3)_2]_3$) was difficult due to its high boiling point and low vapor pressure. An extinguishment value of 8.7 volume % was obtained.

Tris(2,2,2-trifluoroethyl)phosphite was tested at a chamber temperature of 200 °C. An extinguishing value of 1.8 volume % was obtained.

Trimethylphosphite was also blended with either HFC-227ea or HFC-125 to form a nonflammable mixture, and cup burner flame extinguishment concentrations were determined (Table 7–33). These mixtures were 1 % to 2 % lower in extinguishment concentration than the respective pure HFC.

Table 7–33. Flame Extinguishment Values for Trimethylphosphite Blends with HFCs.

Compound Name (/Blend)	Formula	Extinguishment Value, volume %
1,1,1,2,3,3,3-Heptafluoropane (HFC-227ea)	CF_3CHFCF_3	6.2
Trimethylphosphite/HFC-227ea (7.2 %/92.8 %)	$P(OCH_3)_3/CF_3CHFCF_3$	5.1
Pentafluoroethane (HFC-125)	CHF_2CF_3	8.7
Trimethylphosphite/HFC-125 (12.2 %/87.8 %)	$P(OCH_3)_3/CHF_2CF_3$	6.8

From these data, it was concluded that highly fluorinated PCCs in this family can have flame extinguishment efficiencies comparable to halon 1301. While blending flammable PCCs with an HFC might reduce the flammability hazard, the flame extinguishment concentration was dominated by the HFC, and the mixture concentration offered little advantage over the HFC alone. Moreover, during the discharge process, disproportionation of the mixture is likely, potentially creating a zone in which a flammable PCC concentration exists.

Second Series Compound Availability and Synthesis

This first set of results led to the selection of a second set of phosphorus-containing compounds for examination. In this process, compounds such as PH_3 or $P(CH_3)_3$ were ruled out as being flammable, while compounds involving P-F bonds were ruled out due to expected hydrolysis and unacceptable toxicity. The selected compounds represented a range of related structures and included both phosphine and phosphonate compounds. Including both P(III) and P(V) phosphorus oxidation states, as well as incorporating, where possible, similar fluorinated substituents increased the probability of identifying promising chemical families. Promising compounds would serve as guides to future research and compound synthetic efforts.

Each of the selected compounds needed to be synthesized for the NGP. This was accomplished using utilizing bench top and vacuum line procedures. Each of the products was purified and then characterized, as needed for structure verification, by ^{19}F, ^{31}P and ^{13}C NMR, infrared and mass spectral measurements and by elemental analysis. The syntheses performed, as well as relevant literature references, are briefly described below. Table 7–37, at the end of the section, summarizes the results.

Phosphites (Phosphonates) and Phosphates

The most problematic features of these families of PCCs were high boiling points and flammability. Fluorination reduced both. Thus, the most promising additional compounds have formulas such as $P(OR_f)_3$ or $O{=}P(OR_f)_3$, where R_f is a fluorinated group, which should have as low a molecular weight and as high a degree of fluorination as possible. Based on this, two logical compounds for further examination were tris(trifluoromethyl)phosphite ($P(OCF_3)_3$) and tris(trifluoromethyl)phosphate ($O{=}P(OCF_3)_3$).

The phosphite was not commercially available, and efforts to obtain a custom synthesized sample were unsuccessful. Protonated phosphites can be synthesized by reaction of PCl_3 with ROH. Unfortunately, alcohols that could be used to prepare esters containing fluorine bound to the carbon atom adjacent to oxygen are inherently unstable, breaking down by a 1,2-elimination of hydrogen fluoride (HF) to give carbonyl compounds. Alternative synthetic processes were proposed, but with no laboratory willing to undertake the effort.

- Reaction of trifluorophosphine with carbonyl fluoride: $PF_3 + 3\ O{=}CF_2 \rightarrow P(OCF_3)_3$. The enthalpy of reaction (ΔH_r) was estimated based on published bond energy values.[212,213,214] Table 7–34 provides data used in these calculations. The column marked “Basis” indicates the type of compound or types of compounds used to determine the bond energy. ΔH_r was estimated as 92 kJ/mol (22 kcal/mole). Thus, the reaction is slightly endothermic, and the reverse reaction may provide a pathway for decomposition. This is particularly likely since the entropy of the decomposition reaction would almost certainly be positive due to the increase in the number of moles of gas. (Were the material to be formed as the phosphonate structure, $O{=}P(CF_3)(OCF_3)_2$, the reaction is less endothermic, with ΔH_r estimated as to be 58 kJ/mol (14 kcal/mole). Again, however, the reverse reaction should have a positive entropy change. Even though the reactions are predicted to be endothermic, one must recognize that the use of average bond energies is highly suspect.)
- Reaction of phosphorous acid with trifluoromethyl iodide: $P(OH)_3 + 3CF_3I \rightarrow P(OCF_3)_3 + 3HI$.

A synthesis for the phosphate has been published, based on oxidation of tris(trifluoromethyl)phosphine ($P(CF_3)_3$).[215] It has a boiling point of 52 °C at 101 kPa and a melting point of -86 °C. The vapor pressure, p, in kPa can be fit to the equation $\log_{10}p = -1445/T + 4.45$, where T is in K, yielding a vapor pressure of 40 kPa (0.4 atm) at 25 °C. This vapor pressure is sufficient for cup burner testing, but the value at -40 ºC of 0.02 kPa is far too low for aircraft use. An NGP attempt to produce this compound was unsuccessful.

Table 7–34. Enthalpy of Reaction for $PF_3 + 3\ O{=}CF_2 \rightarrow P(OCF_3)_3$.

Bond				ΔH, Total for Bond Formation or Dissociation
Type	**Number**	**Energy, kJ/mol (kcal/mol)**	**Basis**	**kJ/mol (kcal/mol)**
Reactants				
P-F	3	498 (119)	PF_3	1500 (360)
C-F	6	490 (117)	CF_4	2900 (700)
C=O	3	749 (179)	Ketones	2200 (550)
			Sum	6700 (1600)
Product, Phosphite Structure				
P-O	3	368 (88)	P_4O_6	1100 (260)
C-F	9	490 (117)	CF_4	4400 (1050)
C-O	3	358 (85.6)	Organics	1070 (260)
			Sum	6600 (1600)
Product, Phosphonate Structure				
P-O	2	368 (88)	P_4O_6	740 (180)
P=O	1	456 (109)	$O{=}PCl_3$	460 (110)
P-C	1	306 (73)		310 (70)
C-F	9	490 (117)	CF_4	4490 (1100)
C-O	2	358 (85.6)	Organics	720 (170)
			Sum	6600 (1600)

Attention then focused on four phosphite/phosphonate compounds.[iii]

- **Tris(trifluoromethyl) Phosphonate, $O{=}P(CF_3)_3$** (Compound 1, Table 7–37). This two-step synthesis (Reactions 7-43 and 7-44) involved reaction of red phosphorus with CF_3I, forming the flammable intermediate $(CF_3)_3P$. This was followed by an oxidation insertion reaction with nitrous oxide and nitrogen dioxide to form the phosphonate, $(CF_3)_3P{=}O$.[38]

$$\text{Red Phosphorus} + CF_3I\ (232\ °C,\ 60\ hr) \longrightarrow P(CF_3)_3,\ (52\ \%\ \text{yield}) \qquad (7\text{-}43)$$

$$P(CF_3)_3 \xrightarrow{(N_2O,\ NO_2)} (CF_3)_3P{=}O \quad (100\ \%\ \text{yield}) \qquad (7\text{-}44)$$

- **Tris(2,2,2-trifluoroethoxy) Phosphite, $P(OCH_2CF_3)_3$** (Compound 2, Table 7–37). This synthesis was carried out by adding trifluoroethanol dropwise into a vigorously stirred solution of phosphorus trichloride (slight excess) at 0 ˚C. After 5 h, fractional distillation gave the desired product. This reaction is summarized in Reaction 7-45.

$$PCl_3 + CF_3CH_2OH \longrightarrow P(OCH_2CF_3)_3 \quad (100\ \%\ \text{yield}) \qquad (7\text{-}45)$$

- **Bis(trifluoromethyl) trifluoromethoxy Phosphonate, $O{=}P(OCH_3)(CF_3)_2$**, (Compound 3, Table 7–37**)**. The $(CF_3)_2POCF_3$ intermediate was oxidized with a slight molar deficiency of nitrogen dioxide as in the synthesis of Compound l. The NO was removed under vacuum. This reaction is summarized in Reaction 7-46.

[iii] Rearrangements can occur between the phosphite form, e.g., $P(OR)_2R$, and the phosphonate form, e.g., $O{=}P(OR)R_2$.

$$(CF_3)_2POCF_3 \xrightarrow{(NO_2)} (CF_3)_2P(O)OCH_3 \quad (100\ \%\ \text{yield}) \qquad (7\text{-}46)$$

- **Bis(trifluoromethyl) 2,2,2-trifluoroethoxy Phosphonate, $(CF_3)_2P(O)OCH_2CF_3$,** (Compound 4, Table 7–37). This synthesis is very similar to that for Compound 3. This reaction is summarized in Reaction 7-47.

$$(CF_3)_2POCH_2CF_3 \xrightarrow{NO_2} (CF_3)_2P(O)OCH_2CF_3 \qquad (7\text{-}47)$$

Fluoroalkyl Phosphines

Following the lessons learned from the previous family of compounds, examination of the phosphines focused on the smallest, heavily fluorinated molecules. Table 7–35 shows published data for some of the simplest fully fluorinated organic phosphines.

Table 7–35. Perfluoroalkyl Phosphines.

Compound Formula	T_b (°C)	Properties	Reference
$(CF_3)_3P$	17	Spontaneously flammable	216
$(CF_3P)_4$	Not available	Solid, melting point 66.4 °C	220
$(CF_3P)_5$	190	Not available	220
$(CF_3)_2PP(CF_3)_2$	83 to 84	Flammable	216
$(C_2F_5)_3P$	70	Not available	211

The simplest perfluorinated trialkyl compound is tris(trifluoromethyl)-phosphine ($(CF_3)_3P$), which has been prepared as a mixture with trifluoromethyldiiodophosphine, $(CF_3)PI_2$, and bis(trifluoromethyl)-iodophosphine, $(CF_3)_2PI$, by reaction of phosphorus with trifluoroiodomethane (CF_3I),[216] and also by reaction of tris(diethylamino)phosphine, $P(N(C_2H_5)_2)_3$, with trifluoromethyl bromide ($CBrF_3$, halon 1301) and triphenylphosphite, $O{=}P(OC_6H_5)_3$, in tris(dimethylamino)phosphine oxide, $OP(N(CH_3)_2)_3$, hexamethylphosphor-amide, HMPA).[217] Unfortunately, this material (like some of its complexes[218]) is spontaneously flammable (Table 7–35). The iodide derivatives are exceedingly useful precursors for a number of compounds of interest here; however, even with optimized procedures,[219] the syntheses are difficult, and the reactants and products are hard to handle. Reaction of $(CF_3)_2PI$ with mercury gives the flammable compound tetrakis(trifluoro-methyl)diphosphine $(CF_3)_2PP(CF_3)_2$ [216] and the tetrameric and pentameric cyclic compounds $(CF_3P)_4$ and $(CF_3P)_5$[220] (Table 7–35). The compounds $(CF_3)PF_2$ and $(CF_3)_2PF$ are also known.[221]

The higher molecular weight perfluoroalkyl derivatives are likely to be more stable than the methyl compounds. Tris(pentafluoroethyl)phosphine ($(C_2F_5)_3P$), with a boiling point of 70 °C, has been prepared by reaction of phosphorus trichloride (PCl_3) with ethyl lithium (C_2F_5Li), which can be prepared by reaction of chloropentafluoroethane (C_2F_5Cl) with n-butyl lithium (C_4F_9Li).[211] The procedure, however, has not been published. It has proven impossible to prepare the tris(heptafluoropropyl)-phosphine ($(C_3F_7)_3P$), apparently due to steric hindrance.[222]

A large number of trifluoromethyl-substituted diphosphorus compounds having the general formula $(CF_3)_2PRP(CF_3)_2$, where "R" represents a branched or linear hydrocarbon or fluorocarbon chain, have been synthesized as bidentate ligands starting with $(CF_3)_2PP(CF_3)_2$.[223,224] It has been stated that these compounds are difficult to prepare owing to difficulty in synthesis of the diphosphine precursor.[211] A similar compound has also been prepared: $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$, boiling point 105 °C at 11 kPa.[225] The primary interest in these compounds is as bidentate ligands.[226]

Based on this information, the following three compounds were synthesized for further examination.

- **Bis(trifluoromethyl)methoxy Phosphine, $(CF_3)_2POCH_3$**, (Compound 5, Table 7–37). The intermediate, $(CF_3)_2PI$, formed as one of the products in 25 % yield from the reaction of CF_3I and red phosphorus, was reacted at 25 ˚C with AgCl to form $(CF_3)_2PCl$ at an approximately 100 % yield. The chloride was subsequently reacted with methanol in the presence of triethylamine, substituting the methoxide for the iodine. [38] This reaction is summarized in Reaction 7-48.

$$(CF_3)_2PCl + CH_3OH/(CF_3CH_2)_3N \longrightarrow (CF_3)_2POCH_3\text{, (85 \% yield)} \qquad (7\text{-}48)$$

- **Bis(2,2,2-trifluoroethoxy) trifluoromethyl Phosphine**, **$(CF_3)P(OCH_2CF_3)_2$**, (Compound 6, Table 7–37). This synthesis is very similar to the synthesis of Compound 5. This reaction is summarized in Reaction 7-49.

$$(CF_3)PCl_2 \xrightarrow[\text{2eq } (CF_3CH_2)_3N]{\text{2eq } CF_3CH_2OH} (CF_3)P(OCH_2CF_3)_2 \qquad (7\text{-}49)$$

- **Bis(trifluoromethyl) 2,2,2-trifluoroethoxy Phosphine**, **$(CF_3)_2POCH_2CF_3$**, (Compound 7, Table 7–37). This synthesis, very similar to Reaction 7-49, is summarized in Reaction 7-50.

$$CF_3)_2PCl \xrightarrow[(CF_3CH_2)_3N]{CF_3CH_2OH} (CF_3)_2POCH_2CF_3 \qquad (7\text{-}50)$$

Amino Fluoroalkylphosphines

Aminobis(trifluoromethyl)phosphines ($(CF_3)_2PNR_2$, R= -H, $-CH_3$) have been prepared by reaction of chlorobis(trifluoromethyl)phosphine ($(CF_3)_2PCl$) with the appropriate amine.[227] Though these materials are relatively stable liquids (Table 7–36), they are readily oxidized in air. The simplest amino compound is spontaneously flammable, as is the $(CF_3)_2PCl$ starting material. Amines containing two and three bis(trifluorophosphine) groups[228] and compounds of the type $[(CF_3)_2N]_nP(CF_3)_{3-n}$, n = 1 to 3 (the latter discussed further in Reference 93) have also been prepared (Table 7–36). The starting materials, however, are also spontaneously flammable: $(CF_3)_2PCl$ or tris(trifluoromethyl)phosphine ($(CF_3)_3P$). Aminobis-(heptafluoropropyl)-phosphine ($(C_3F_7)_2PNH_2$), a high boiling liquid (Table 7–36), has been prepared by reaction of $(C_3F_7)_2PCl$ with anhydrous ammonia.[222] As is typical for all of these reactions, the starting material was prepared by reaction of heptafluoropropyl iodide with phosphorus at high temperature and pressure followed by replacement of the iodide with chloride using silver chloride.

The volatility of even the simplest of these compounds was insufficient for aircraft use, and this chemical family was not examined further.

Table 7–36. Amino Fluoroalkylphosphines.

Compound Formula	T_b (°C)[a]	Properties	Reference
$(CF_3)_2PNH_2$	67.1	Spontaneously flammable	227
$(CF_3)_2PNH(CH_3)$	72.3	Not available	227
$(CF_3)_2PN(CH_3)_2$	83.2	Not available	227
$((CF_3)_2P)_2NH$	Not available	Vapor pressure 6.2 kPa at 23.9 °C	228
$((CF_3)_2P)_2NCH_3$	Not available	Vapor pressure 2.3 kPa at 25.0 °C	228
$((CF_3)_2P)_3N$	Not available	Solid, melting point 36.5 ºC to 36.8 °C	228
$(CF_3)_2NP(CF_3)_2$	51	Stable at room temperature	229
$((CF_3)_2N)_2P(CF_3)$	92.5	Stable at room temperature	229
$((CF_3)_2N)_3P$	135	Stable at room temperature	229
$(C_2F_7)_2PNH_2$	143	Not available	222

[a] 101 kPa (nominal) pressure.

Reactivity in Air

Upon breaking open their respective glass sealed vials, Compounds 5 and 7 reacted extremely vigorously (i.e., fumed) as air entered and contacted the liquid agent. Some fuming was also noted for Compounds 3 and 6. It may be that compound 7 underwent air oxidation to yield a phosphonate structure, $O{=}P(OCH_2CF_3)(CF_3)_2$, or oxygen insertion reactions at the P-CF_3 bonds.

Cup Burner Flame Extinguishment Testing

In view of the wide range of boiling points represented by the compounds synthesized, a means was required for preventing the condensation on cooler surfaces and countering the evaporative cooling effects of the nebulized agent as they dispersed into the air stream of the cup burner. Heating the inlet air to between 50 ºC and 55 ºC counteracted the evaporative cooling effects of the misted agent at the tip of the nebulizer and enhanced droplet vaporization. On mixing with the cooler, nebulized agent/air stream, the column temperature dropped to between 45 ºC to 50 ºC. The preheated air was also employed to warm the entire cup burner chimney prior to a test run, and as a result no condensation of agent was observed during or following extinguishment testing.

Due to the limited quantities of some agents, each was tested no higher than the screening concentration of 5 % by volume.

Observations

It is possible that phosphonates having multiple -CF_3 groups are too stable for the phosphorus atom to be released into the cup burner flame. When Compound 1 was tested at 5 volume %, no evidence of flame lift-off was observed. Compound 3, with two -CF_3 groups, showed lift-off and flame extinguishment just below 5 volume %. Compound 4, also with two -CF_3 groups, showed lift-off but no flame extinguishment at 5 volume %.

Only Compound 4 approached the desired boiling point range. In the trade-off between higher degree of fluorination to reduce the boiling point and moderate hydrogenation for efficient fire suppression, there may be limited further promise in this family of compounds. This conclusion must be tempered by the observed low cup burner test value (1.8 %) of compound 7 and the possibility that air reaction is converting it to a very efficient flame suppressant. It cannot, however, be concluded at this point that the air oxidation produces a complete conversion to a single compound or that the reaction is complete by the time the products enter the flame zone.

In earlier work, Compound 2 had been reported to have a cup burner extinguishment value of 1.78 volume % for n-heptane fuel.[39] This value is much lower than that measured subsequently and reported here. Differences in manner of sample vaporization could well be responsible. In the earlier studies, a hot sand bath (>250 ºC) was employed to volatilize the compound as it was introduced into the base of the cup burner. It is possible this method induced thermal decomposition and air reaction of the test compound, yielding a more effective flame suppressant.

Compound 7, though air reactive, yielded an impressively low cup burner value. It is possible this low value might have been due to a breakdown product whose air concentration was even lower than 1.8 volume %. Identification and study of Compound 7 (or Compound 5) air reaction products might lead to significant advancements in phosphorus-based suppressants for aircraft dry bays and other unoccupied areas. If the extinguishing concentration were 1 volume % or lower, significant improvements in the efficiencies of solid propellant fire extinguishers or powder panels (Chapter 9) might be achieved. The nature and toxicity of compound 6 air decomposition products needs to be determined.

The synthesis attempted of (tris(trifluoromethoxy) phosphonate, $O=P(OCF_3)_3$) had been reported in the literature. While the NGP was unable to obtain this compound, a realistic expectation of its synthesis still exists. Its similarity to the structures thought to be the breakdown products from compound 7, that may be contributing to its demonstrated higher effectiveness, make this compound a prime target for further research and testing.

Phosphines provide good materials for mechanistic studies; however, they can be ruled out as candidates owing to their inherent low stability (many are flammable, sometimes spontaneously, even with fluorinated substituents) and high toxicities. Though it is possible to obtain fire extinguishment (sometimes very efficient) with phosphazenes, these compounds have inherently high molecular weights and, therefore, very low volatility.

Fluoroalkyl (alkoxide) Phosphorus Compounds - Summary

No phosphorus-containing compounds were identified that met needed criteria for volatility, stability, and flame suppression efficiency. Some may be useful flame suppressants at temperatures above the current low temperature criterion. Given the high flame suppression efficiency of a chemically liberated phosphorus atom, a well chosen PCC could enhance the effectiveness of solid propellant fire extinguishers. Determination of the decomposition rates and combustion products could further that choice. Some of the phosphorus compounds are polar or reactive (to hydrolysis) and thus are likely to have short atmospheric lifetimes. The environmental fate of their decomposition products fate would need to be assessed.

Table 7–37. Phosphorus-containing Compound Performance.

	Compound Name	Formula	Mass Available(g)	T_b (°C)[a]	Ext. Conc. (vol. %)	Exposure of Agent to Air
1	Tris(trifluoromethyl) Phosphonate	$O=P(CF_3)_3$	7.3	32	None @ 5 %	No fumes or ignition
2	Tris(2,2,2-trifluoroethoxy) Phosphite	$P(OCH_2CF_3)_3$	50.0	130 (est.)	3.1	No fumes or ignition
3	Bis(trifluoromethyl) trifluoromethoxy Phosphonate	$O=P(OCH_3)(CF_3)_2$	5.5	42	4.6	Fumes, no ignition
4	Bis(trifluoromethyl) 2,2,2-trifluoroethoxy Phosphonate	$O=P(OCH_2CF_3)(CF_3)_2$	7.0	130	None @ 5 %	No fumes, did not ignite cloth
5	Bis(trifluoromethyl)methoxy Phosphine	$P(OCH_3)(CF_3)_2$	5.3	55	Ignited on air exposure[b]	Ignited spontaneously
6	Bis(2,2,2-trifluoroethoxy) trifluoromethyl Phosphine	$P(OCH_2CF_3)_2CF_3$	7.2	111	3.0	Fumes, no ignition
7	Bis(trifluoromethyl) 2,2,2-trifluoroethoxy Phosphine	$P(OCH_2CF_3)(CF_3)_2$	6.5	25	1.8	Ignited cloth, fumed strongly

a. Determined at nominally 100 kPa, except Compound 7 at 7 kPa.

b. In view of the low cup burner test value of Compound 7, the structurally similar Compound 5 was preserved in order to provide a future opportunity to identify the product of its reaction with air.

7.4.5 Fluoroalkyl Nitrogen-based Candidates

Atmospheric Lifetime, ODP, and GWP

The fact that nitrogen oxides could be direct depleters of stratospheric ozone was recognized earlier than that halocarbons posed an environmental threat.[230] The first concerns were about direct injection of nitrogen oxides into the stratosphere by high altitude aircraft.[231] Nitrogen compounds, however, play other roles in atmospheric chemistry involving ozone depletion. The ozone chemical balance depends directly on the total amount of active nitrogen species.[232] Nitric oxide (NO) releases chlorine from chlorine monoxide (Reaction 7-52).[233] Nitrogen oxides can also decrease stratospheric ozone depletion by the formation of the chlorine nitrate ($ClONO_2$) reservoir (Reaction 7-53)[233] and by the removal of •OH (Reactions 7-54 through 7-56).[234] Hydroxyl free radicals convert HCl and HBr to free chlorine and bromine atoms, which are potent depleters of stratospheric ozone. Removal of nitric acid by condensation is believed to play a major role in the Antarctic ozone hole.[234]

$$\bullet NO + \bullet ClO \rightarrow Cl + \bullet NO_2,\ \Delta H_r = -37\text{ kJ/mole},\ \Delta G_r = -28\text{ kJ/mole} \qquad (7\text{-}52)$$

$$\bullet NO_2 + \bullet ClO \rightarrow ClONO_2 \qquad (7\text{-}53)$$

$$\bullet OH + HNO_3 \rightarrow H_2O + \bullet NO_3 \qquad (7\text{-}54)$$

$$\bullet NO_3 + h\nu \rightarrow \bullet NO_2 + \bullet O \qquad (7\text{-}55)$$

$$\bullet OH + \bullet NO_2 + M \rightarrow HNO_3 + M^*,\ \Delta H_r = -206\text{ kJ/mole},\ \Delta G_r = -159\text{ kJ/mole} \qquad (7\text{-}56)$$

Since some highly fluorinated amines have long atmospheric lifetimes, it is possible that anthropogenic amines of interest in this research could deplete stratospheric ozone.

A relatively large amount of data are available for reactions of atmospheric •OH radicals with nitrogen-containing compounds; however, few experimental data (as opposed to estimations) are available for compounds that might be useful as halon 1301 replacements, i.e., those containing fully or partially fluorinated alkyl groups (to improve toxicity and flammability characteristics). Amines containing no hydrogen atoms are expected to be inert to attack by •OH, which can be seen in the absence of reaction observed with N,N-bis(pentafluoroethyl)penta-fluoroethanamine ($N(CF_2CF_3)_3$), for which an •OH rate constant $k_2 < 6 \times 10^{-16}$ cm^3/molec-s has been reported.[235] This rate constant corresponds to an estimated atmospheric lifetime of greater than 55 years.

A relatively large amount of data is available for hydrogen-containing, nonfluorinated amines. Nitroalkanes (RNO_2) have been relatively well studied,[236] but these have little resemblance to amines, which are the most promising of the nitrogen-containing halon replacements. As a result of concerns about health impacts, the atmospheric chemistry of N-nitrosodimethylamine ($(CH_3)_2N$-NO) and dimethylnitramine ($(CH_3)_2N$-NO_2) has been examined.[237] Table 7–38 presents rate constants for hydroxyl free radicals reactions with several nonfluorinated amines.[119] Where several values were given, the first value cited at or near 298 K was used for consistency. These values were calculated at or near the high pressure limit. Atmospheric lifetimes in Table 7–38, calculated from a globally tropospheric •OH concentration of 9.7 x 10^5 molecules/cm^3, are on the order of a few days or less. The reactions of all of the compounds in Table 7–38 probably involve hydrogen atom abstraction from the alkyl groups. Since all of these compounds are highly polar, rainout would also be an effective removal mechanism.

Rate constants have been compiled for gas-phase reactions of O_3 with a number of nitrogen-containing compounds,[238] and the data for amines are shown in Table 7–39. The rate constants increase and lifetimes (estimated from the globally averaged tropospheric O_3 concentration) decrease with increasing alkyl substitution. This is also the direction of increasing proton affinity (-ΔH for the reaction $B + H+ \rightarrow BH+$, where B is a base).[239]

Table 7–38. •OH Rate Constants for Nitrogen-containing Compounds.

Compound Name	k_{OH}, cm^3/molec-s	Temperature (K)	Atmospheric Lifetime (days)[a]
Methylamine, $NH_2(CH_3)$	$22.0 \pm 2.2 \times 10^{-12}$	299	0.5
Ethylamine, $NH_2(CH_2CH_3)$	$27.7 \pm 2.8 \times 10^{-12}$	299.6	0.4
Dimethylamine, $NH(CH_3)_2$	$64.5 \pm 6.6 \times 10^{-12}$	298.5	0.2
Trimethylamine, $N(CH_3)_3$	$60.9 \pm 6.1 \times 10^{-12}$	298.7	0.2
Diethylhydroxylamine $N(CH_2CH_3)_2OH$	101×10^{-12}	308	0.1
2-(Dimethylamino)ethanol $CH_2(N(CH_3)_2)CH_2OH$	$47 \pm 12 \times 10^{-12}$	300 ± 2	0.3
2-Amino-2-methyl-1-propanol $CH_3C(CH_3)(NH_3)CH_2OH$	$28 \pm 5 \times 10^{-12}$	300 ± 2	0.4
N-Nitrosodimethylamine $(CH_3)_2N$-NO	$02.53 \pm 0.21 \times 10^{-12}$	298 ± 2	4.7
Dimethylnitramine, $(CH_3)_2N-NO_2$	$03.84 \pm 0.15 \times 10^{-12}$	298 ± 2	3.1

a Based only on reaction with •OH.

Table 7–39. Rate Constants for Reactions of O_3 With Amines.

Compound Formula	k_2 at 296 K, (cm^3/molec-s)	Estimated Tropospheric Lifetime (days)	Proton Affinity (kJ/mole)
$NH_2(CH_3)$	$2.13 \pm 0.29 \times 10^{-20}$	1087	896
$NH_2(CH_2CH_3)$	$2.76 \pm 0.34 \times 10^{-20}$	839	908
$NH(CH_3)_2$	$2.61 \pm 0.30 \times 10^{-18}$	008.9	923
$N(CH_3)_3$	$9.73 \pm 1.02 \times 10^{-18}$	002.4	938

The reactions appear to proceed by addition of O_3 to the nitrogen to give R_3N+-O-O-O-, which then decomposes by uncertain mechanisms. Data for reactions involving halogen-substituted alkyl amines have not been reported; however, it is likely that the reaction rates will decrease with increasing halogen substitution, which makes the nitrogen atom less electron rich.

Rate constants have also been reported for reaction of O_3 with pyridines (approximately 5 x 10^{-20} cm^3/molec-s to 50 x 10^{-20} cm^3/molec-s) and for unsaturated nitriles (< 1 x 10^{-19} cm^3/molec-s to 1.38 x 10^{-19} cm^3/molec-s for acrylonitrile CH_2=CHCN and 3.52 x 10^{-19} cm3/molec-s for methacrylonitrile $CH_2=C(CH_3)CN$).[121] Ozone is known to react with alkene derivatives, and the results for the acrylonitriles probably have little to do with the presence of nitrogen. The pyridines, which are, at best, distantly related to the amines of interest, have calculated lifetimes for reaction with tropospheric ozone of approximately 1 year or less. The maximum values of the rate constants for reaction of N-nitrosodimethylamine $(CH_3)_2N\text{-}NO$ and dimethylnitramine $(CH_3)_2N\text{-}NO_2$ with tropospheric ozone are 1×10^{-20} cm^3/molec-s and 3×10^{-21} cm^3/molec-s (calculated lifetimes of 6 years and 21 years, respectively) and could be less than this.[237] Photolysis is probably the primary removal mechanism for N-nitrosodimethylamine.

Of particular interest for fire suppression are alkyl-substituted amines, with one or more alkyl groups containing bromine atoms. The primary problem is that fluorination is needed to decrease both the flammability and toxicity of amines. As fluorination increases, both the polarity and the flammability are expected to decrease (for different reasons). The polarity is directly related to toxicity, since highly polar amines are strong bases and therefore irritants. The polarity is, however, also directly related to the effectiveness of atmospheric removal. Nonfluorinated amines are expected to undergo significant rainout.

Reported lifetimes and GWPs were reviewed for several fluoroalkyl amines in Reference 240. However, the values are highly suspect. For example, the lifetime of $(CH_3)_2NC_2F_5$ is reported as 250 years, while that of the much less hydrogen-rich compound $(CF_3)_2NCF_2CF_2H$ is given as 2.10 years.[241] Moreover, the estimation methods for the lifetimes and GWPs were not reported. Eliminating the highly questionable value of 250 years gives estimated lifetimes for hydrofluoroamines (HFAs) of around 0.3 years to 3 years.[241]

While there is nothing inherent in nitrogen compounds that would lead to atmospheric lifetime or GWP problems, individual compounds may have significant effects. Replacement of fluorine atoms with bromine atoms would tend to reduce HFA lifetimes by a factor of 10 in some compounds. Data indicate that for bromine-containing alkanes, each 10-year increase in the atmospheric lifetime increases the ODP by approximately a factor of 2. Therefore, hydrofluorobromoamines should have low ODPs. Any impact from nitrogen on stratospheric ozone would be negligible compared to that from bromine.

Research from the National Industrial Research Institute of Nagoya has focused on fluoroalkylamines, with an emphasis on perfluoroalkyl derivatives, as fire suppressants.[242] All of their fluoroalkylamines inhibited flame propagation less efficiently than CF_3Br, but more efficiently than HFC-227ea. A thorough assessment of the atmospheric impact of fluorinated amines and of bromofluoroamines (based on estimations and calculations) has been presented.[240] For example, the compound $(CBrF_2)(CF_3)NCH_3$ is estimated to have an atmospheric lifetime of 10 days and an ODP of 0.006 relative to CFC-11.[240] The amine $N(CF_3)_2CF{=}CF_2$ is expected to have a lower atmospheric lifetime due to the presence of its $\text{-}F{=}CF_2$ group.

Toxicity

The acute inhalation toxicities of some hydrofluoroamines (HFAs) are given in Table 7–40.[29] These have also been reviewed in Reference 240; however, here the LC_{50} values are also given as volume percent. Although these lower bounds do not cause any concern, measurements at higher concentrations are needed. In addition to the compounds shown in Table 7–40, the LC_{LO} for mouse inhalation has been reported as 0.0123 volume % for 2,2,2-trifluoroethylamine $(CF_3CH_2)NH_2$,[67] a value that appears rather low; however, this compound contains hydrogen atoms directly bonded to the nitrogen.

Table 7–40. Acute Inhalation Toxicity of Hydrofluoroamines.

Compound Formula	Exposure Time, Subject	LC_{50} (mg/L)	Molecular Weight	LC_{50} (volume %)
$(CF_3)_2NCH_3$	3 h, rat	>20	113.99	>0.43
$(CF_3)_2NCF_2CF_2H$	3 h, rat	>20	253.04	>0.19
$(CF_3)_2NCFHCF_3$	3 h, rat	>20	253.04	>0.19
$(CF_3)_2NCH_2CF_3$	3 h, rat	>20	235.05	>0.21
$(CF_3)_2NCH_2CF_2H$	4 h, rat	>20	217.06	>0.23
$(CF_3)_2NCH_2CH_3$	4 h, rat	>20	181.08	>0.27

A review of Reference 67 identified inhalation toxicity data for over 120 compounds containing both nitrogen and fluorine; however, inhalation data are available for only 6 of these (Table 7–41). Nearly every compound in this limited set is given a SAX HR of 3, signifying the worst hazard level. However, none of these compounds is closely related to amines, and most contain groups known to lead to toxicity. Many N-nitroso compounds, such as the nitrosocarbamates, are carcinogens.

Table 7–41. Toxicity and Safety Information for Selected N, F Compounds.

Compound Name	Formula	CAS No.	Observations [a]
fluoroacetanilide	C_8H_8FNO	330-68-7	{RTECS AE2975000} [FFH000] LC_{LO} (mouse, inh, 10 min) = 480 mg/m^3. Poison by ingestion, intraperitoneal, and possible other routes. Moderately toxic by inhalation. HR = 3.
beta-fluoroethyl-N-(beta-chloroethyl)-N-nitrosocarbamate	$C_4H_8ClFN_2O_3$	63884-92-4	{RTECS EZ2275000} [IH000] LC_{LO} (guinea pig, inh, 10 min) = 300 mg/m^3. Poison by inhalation. HR = 3.
2-fluoroethyl-N-methyl-N-nitrosocarbamate	$C_4H_7FN_2O_3$	63982-15-0	{RTECS FC6475000} [FIS000] LC_{LO} (guinea pig, inh, 10 min) = 100 mg/m^3, LC_{LO} (mouse, inh, 10 min) = 500 mg/m^3. Poison by inhalation. HR = 3.
3-nitrobenzotrifluoride	$C_7H_4F_3NO_2$	98-46-4	RTECS XT3500000} [NFJ500] LC_{50} (rat, inh) = 870 mg/kg, LC_{50} (mouse, inh, 2 hr) = 880 mg/m^3. Moderately toxic by ingestion, inhalation, and subcutaneous routes. HR = 3.
(alpha, alpha, alpha-trifluoro-*m*-tolyl)isocyanate	$C_8H_4F_3NO$	329-01-1	RTECS NR200000} [KJ250] LC_{50} (rat, inh) = 3600 mg/m^3, LC_{50} (mouse, inh) = 3300 mg/m^3. Moderately toxic by ingestion, inhalation, intraperitoneal routes. HR = 2.
2,4,6-trifluoro-s-triazine	$C_3F_3N_3$	675-14-9	{RTECS XZ1750000} [TKK000] LC_{50} (rat, inh, 4 hr) = 3.1 µL/L. Poison by skin contact, inhalation. HR = 3.

[a] The SAX No. (Reference 67) is given in brackets followed by information from that reference; the RTECS No. (Reference 138) is given in braces. “HR” denotes the SAX Hazard Rating.

No generalities on the toxicity of nitrogen compounds can be made. Amines range in toxicity from poisons to only slightly toxic. In fact, fully fluorinated alkyl amines show no toxicity. Some amines are skin irritants while others are sensitizers.[67] Although LC_{50} values have been determined for some hydrofluoroamines (HFA), the test levels are very low and measurements at higher concentrations are needed. ($(CH_3)_2NCF_2CBrF_2$) has tested negative for genotoxicity and cytotoxicity.[243]

Volatility

Generally due to toxicity concerns, the only compounds of interest are amines containing three alkyl groups. Moreover, to decrease toxicity and corrosivity (by decreasing polarity) and to decrease flammability, the alkyl groups should be at least partially fluorinated. This chemical family represents a very broad range of fluorination patterns and alkyl substitution patterns. Table 7–41 indicates that there are some such fluoroalkylamines with boiling points below and near the screening criterion.

Flame Extinguishment

As the primary question to be addressed was extinguishment performance, and little change in performance was expected amongst the fully fluorinated ethyl and methyl amines, three low boiling compounds were selected for examination.

Table 7–42. Fluoroalkylamine Boiling Points.

Compound Formula	T_b (°C)
$N(CF_3)_3$	-10
$N(CF_3)_2CF{=}CF_2$	13.7
$N(CF_3)_2CH_3$	11 to12
$N(CF_3)_2CF_2CF_5$	20.5
$N(CF_3)_2CF_2CHF_2$	32.0
$N(CF_3)_2CH_2CH_3$	33 to 34
$N(CF_3)_2CH_2CH_3$	33.3
$N(CF_3)_2CH_2CF_3$	38
$N(CF_3)(CF_2CF_3)_2$	46

- **N,N-bis(trifluoromethyl)pentafluoroethanamine ((pentafluoroethyl)bis(dimethyl)-amine, $N(CF_3)_2(C_2F_5)$)**, obtained from Dr. Takashi Abe, National Industrial Research Institute (NIRI), Japan was the product of electrochemical fluorination.[244] This synthetic approach is generally not amenable to the preparation of partially fluorinated compounds. Three cup burner tests were run to give an average extinguishment value of 3.8 volume %.
- **Trifluoroacetonitrile**, **CF_3CN**, is a commercially available compound.[170,192] It has very low boiling point of -67 °C and seeming potential tropodegradability resulted in an interest in further study. Cup burner tests yielded flame extinguishment at 9 volume %, suggesting that there is no chemical effect from the nitrile group.
- **N,N-bis(trifluoromethyl)-trifluoro-methanamine (tris(trifluoromethyl)amine, $N(CF_3)_3$)**, synthesis was attempted unsuccessfully using the procedure shown in Reaction 7-57. No cup burner value therefore was obtained.

$$NH_3 + 3CF_3I \rightarrow N(CF_3)_3 + 3HI \qquad (7\text{-}57)$$

Summary

There is no indication that the presence of a nitrogen atom in a compound significantly improves the fire suppression efficiency relative to other thermally active flame suppressants. The fully fluorinated compounds, which have the lower boiling points, are also likely to have long atmospheric lifetimes. While partially fluorinated amines are likely to have relatively short atmospheric lifetimes, it is difficult to determine whether the lifetime would be sufficiently short to allow bromine substitution (to increase flame suppression efficiency). Toxicity appears to be problematic for the partially fluorinated compounds.

7.4.6 Bromofluoroalkyl Nitrogen-based Candidates

There are three families of this type that were considered: amines, imines, and nitriles.

In general, the atmospheric lifetimes of bromofluoro nitrogen-based compounds were expected to be similar to those of analogous non-brominated nitrogen-based compounds. There is no indication that the nitrogen alkyl linkage provides any significant contribution to rainout. The polarity of the nitrogen lone pair may be too small. Perfluorinated saturated amines are expected to have atmospheric lifetimes similar to those of the perfluorinated alkanes, a property that generally makes their use as halon replacements questionable. The atmospheric lifetimes for partially fluorinated amines are much shorter. Atmospheric lifetimes of imines are unknown but may well be limited by their unsaturated bond, though this has not been confirmed. Bromination of the amine or imine structures is not expected to alter this assessment. Cup burner flame extinguishment results suggested that a wide number of these compounds would likely meet extinguishment performance needs.

The toxicity of bromofluoro nitrogen based compounds was expected to be higher than those of analogous non-brominated nitrogen-based compounds.

Bromofluoroamines

Amines offer significant promise, particularly as a result of research underway in Japan on the applications of fluoroalkyl amines as halon and CFC replacements.[244] Much of this research appears to be headed toward perfluoroalkyl amines, which are likely to have long atmospheric lifetimes. Nevertheless, the work provides synthetic routes and property evaluations. Incompletely halogenated compounds, such as $N(CF_3)(CHF_2)(CF_2Br)$, could provide short atmospheric lifetimes and chemical suppression.

Bromofluoro amines have a wide range of structures, as indicated by the examples in Table 7–43.

Table 7–43. Bromofluoroamine Candidate Compounds.

Chemical Formula		
$N(CF_3)_2CFHBr$	$N(CF_2H)(CF_2H)(CFHBr)$	$N(CFH_2)(CFH_2)(CF_2Br)$
$N(CF_3)(CF_2H)CF_2Br$	$N(CFH_2)(CF_3)(CFHBr)$	$N(CFH_2)(CF_2H)(CFHBr)$
$N(CF_3)(CF_2H)CFHBr$	$N(CF_3)(CF_2H)(CH_2Br)$	$N(CH_3)(CF_3)(CFHBr)$
$N(CF_2H)(CF_2H)CF_2Br$	$N(CH_3)(CF_3)(CF_2Br)$	$N(CH_2F)(CF_3)(CH_2Br)$
$N(CFH_2)(CF_3)CF_2Br$	$N(CH_3)(CF_2H)(CF_2Br)$	

There are synthetic pathways to many of these. For instance, N-bromobistrifluoromethylamine $(CF_3)_2NBr$ adds to the unsaturated compounds tetrafluoroethene $CF_2=CF_2$, trifluoroethene $CHF=CF_2$, 1,1-difluoroethene $CH_2=CF_2$, cis-1,2-difluoroethene $CHF=CHF$, ethene $CH_2=CH_2$, hexafluoropropene $CF_2=CFCF_3$, chlorotrifluoroethene $CClF=CF_2$, and 1,2-dichlorodifluoroethene $CClF=CClF$ under mild conditions, to give the 1:1 adducts in high yield. The $(CF_3)_2N$ attaches only to the CH_2 group of 1,1-difluoroethene, whereas trifluoroethene gives the isomers $(CF_3)_2NCHFCF_2Br$ (78 %) and $(CF_3)_2NCF_2CHFBr$ (22 %). Hexafluorocyclobutene and octafluorobut-2-ene require more drastic conditions, and give the olefin dibromide and tetrakistrifluoromethylhydrazine rather than addition of the N-bromo-compound.[245]

The boiling points of bromofluoroamines range only as low as 22 º C, as indicated in Table 7–44. In the last three rows, the flame extinguishment values for the two compounds and their mixture indicate that the value of the bromine atom and the thermal effects of the complex molecule were both realized. However, because of the N-Br linkage, the lowest boiling of these compounds may be unacceptably toxic.

Table 7–44. Bromofluoroamine Boiling Points and Flame Suppression Results.

Chemical Formula	T_b (°C)	Cup Burner Flame Extinguishment (Volume %)
$(CF_3)_2N\text{-}Br$	22	---
$(CF_3)_2NCBrF_2$	40.6	---
$(CF_3)_2NCF_2CBrF_2$	59.5	---
$N(CF_3)_2(CHFCF_2Br)$	72	2.4
60 % $N(CF_3)_2(CHFCF_2Br)$, 40 % $N(CF_3)_2(CF_2CFHBr)$	72	2.4
$N(CF_3)_2(CH_2CF_2Br)$	80	2.4

Imines

Bromofluoroimines were until recently unstudied. This is in large measure due to a lack of availability of starting materials and facilities willing to attempt the chemistry. Synthetic approaches to some compounds have been developed and reported.[246,247,248]

The simplest of these, N-bromo-difluoromethanimine, $CF_2=NBr$, has an attractively low boiling point of 14 ºC. However, it too has an N-Br linkage and may be unacceptably toxic.

Nitriles

As seen in the prior section for CF_3CN, it is unlikely that nitriles would have an intrinsic chemical fire suppression capability. The addition of bromine or iodine should impart a chemical flame suppression contribution.

Bromodifluoroacetonitrile (CF_2BrCN) was the sole brominated fluoroalkyl nitrile obtained for examination. Its boiling point is uniquely low, 3 ºC, which is also the lowest boiling potentially tropodegradable brominated compound identified. Cup burner testing of CF_2BrCN indicated an upper bound flame extinguishment value of 4 volume %, consistent with the effect of the bromine atom and confirming the minor impact of the triple bond on flame extinguishment efficiency. There was an unconfirmed report that this compound is toxic. Should the minimum in-flight temperature requirement be relaxed, toxicity and atmospheric lifetime determinations for this compound would be in order.

7.4.7 Fluorinated Ethers

Fire Suppression Properties

Hydrofluoropolyethers (HFPE) are being introduced into the market, and there is some evidence for relatively good fire suppression performance.[249] A large amount of research has been performed on fluoroethers as CFC replacements.

Atmospheric Lifetimes, ODP, and GWP

The presence of the ether linkage increases reactivity toward hydrogen abstraction, though fluorine substitution decreases the enhancement.[250] Hydrofluorocarbons show an approximately linear correlation between k_{OH} and the highest-occupied molecular orbital (HOMO) energies.[251] Rate constants, many estimated, reported for reaction of hydrofluoroethers (HFE) with •OH are shown in Table 7–45. In the absence of a hydrogen atom, fluorinated ethers exhibit no reaction with •OH, significantly increasing the atmospheric lifetime.

Very little work has been done on reactions of ethers with ozone, primarily due to their low reactivity. The rate constants for reaction with furan (2.42×10^{-18} cm^3/molec-s) and 2,5-dihydrofuran (1.61×10^{-17} cm^3/molec-s) are relatively large, owing to the presence of a double bond.[238] For saturated ethers, however, rate constants are expected to be extremely slow, $\leq 10^{-20}$ cm^3/molec-s, at room temperature.[238]

The energy of the HOMO has been used to estimate atmospheric lifetimes for a number of HFEs.[252] A list of atmospheric lifetimes reported for halogenated ethers, most of which are estimated, Table 7–46.

The degradation products resulting from the alkoxy radicals formed after initial hydrogen atom abstraction from hydrofluoropolyethers (HFPE) have been studied.[253] Chlorine-atom initiated photooxidations of the HFPEs in air ($HCF_2OCF_2OCF_2OCF_2H$, $HCF_2OCF_2CF_2OCF_2H$ and $HCF_2OCF_2OCF_2H$) produced COF_2 as the only carbon-containing product, with observed average COF_2 molar formation yields of 4.73, 3.77, and 2.82, respectively. In the early stages of the reaction, the COF_2 molar formation yields are close to the number of carbon atoms in each parent HFPE. Based on current knowledge of degradation pathways of hydrofluorocarbons (HFC) and hydrochlorofluorocarbons (HCFC), it is expected that COF_2 will also be produced with near-unit yield per carbon atom from the above HFPEs in the troposphere, where loss processes would be initiated primarily by reaction with •OH radicals.

Toxicity

The toxicity of ethers is relatively low, and the ether linkage has a relatively low biological and chemical reactivity.

Table 7–45. Rate Constants for Hydrofluoroether Reactions with •OH.

Halocarbon No.	Formula	k_{OH}, cm^3/molec-s	Reference
HFE-CE225ea	-O-CF_2CHFCF_2-	[a]2.51 x 10^{-15}	250
		[a]2.4 x 10^{-15}	250
HFE-E	CH_3-O-$CF(CF_3)_2$	[a,b]1.6 x 10^{-14}	254
HFE-E	CH_3-O-$CH(CF_3)_2$	[a,b]2.2 x 10^{-13}	254
HFE-E	CHF_2-O-$CH(CF_3)_2$	[a,b]1.8 x 10^{-14}	254
HFE-E	CH_2F-O-$CH(CF_3)_2$	7.3 x 10^{-14}	255
HFE-E125	CHF_2-O-CF_3	[a]3.38 x 10^{-15} [a]3.56 x 10^{-15} [c]4.2 x 10^{-16}	250 250 249
HFE-E134	CHF_2-O-CHF_2	[a]2.53 x 10^{-14} [a]2.41 x 10^{-14} [a,b]3 x 10^{-15} [c]2.3 x 10^{-15}	2500 250 254 249
HFE-E143a	CH_3-O-CF_3	[a]2.14 x 10^{-14}	250
HFE-E227ca1	CHF_2-O-CF_2CF_3	[b,d]1.95 x 10^{-15}	251
HFE-E227ca2	CHF_2CF_2-O-CF_3	[b,d]4.5 x 10^{-15}	251
HFE-E227ea1	CF_3CHF-O-CF_3	[a,b]5.1 x 10^{-15} [b,d]3.5 x 10^{-15}	254 251
HFE-E236ca1	CHF_2-O-CF_2CHF_2	[b,d]1.15 x 10^{-14}	251
HFE-E236ca12	CHF_2-O-CF_2-O-CHF_2	1.3 x 10^{-15}	249
HFE-E236ea1	CHF_2-O-$CHFCF_3$	[a,b]9.5 x 10^{-15} [b,d]7 x 10^{-15}	254 251
HFE-E236ea2	CHF_2CHF-O-CF_3	[b,d]3 x 10^{-14}	251
HFE-E236mf1	CF_3CH_2-O-CF_3	[a,b]1.5 x 10^{-14}	254
HFE-E245ca2	CHF_2-O-CF_2CH_2F	[b,d]7 x 10^{-15}	251
HFE-E245cb1	CH_3-O-CF_2CF_3	[c]1.07 x 10^{-14} [a,b]4.6 x 10^{-14} [b,d]5.5 x 10^{-14}	256 254 251
HFE-E245cb2	CH_3CF_2-O-CF_3	[b,d]1.5 x 10^{-15}	251

a 296 K
b Estimated from HOMO energy.
c 298 K
d Average

Table 7–46. Atmospheric Lifetimes for Fluorine-containing Ethers.

Halocarbon No.	Chemical Formula	Atmospheric Lifetime (years)	Reference
FE-CE216	-O-$CF_2CF_2CF_2$-	[a]>330	250
HCFE-E235ca2	CHF_2-O-CF_2CHClF	[a]6	255
HCFE-E235da1	CHF_2-O-$CHClCF_3$	[a]5	255
HFE-CE225ea	-O-CF_2CHFCF_2-	[b,c]26	250
HFE-E	CHF_2-O-$CH(CF_3)_2$	[a]3.8	257
HFE-E	CH_3-O-$CF(CF_3)_2$	4.9 [b,c]3.5	257 250

Halocarbon No.	Chemical Formula	Atmospheric Lifetime (years)	Reference
		4.3	258
HFE-E	$CH_3-O-CH(CF_3)_2$	[b,c]0.25	254
HFE-E	$CH_2F-O-CH(CF_3)_2$	[a]1.4	255
		[b,c]3.1	254
HFE-E	$HF_2CO(CF_2O)n(CF_2CF_2O)mCF_2H$	[e]8	f
HFE-E125	CHF_2-O-CF_3	82	259
		19	250
		[b,c]156	249
HFE-E134	$CHF_2-O-CHF_2$	8	259
		[b,c]2.6	250
		[b,c]19	250
		[b,c]35	249
HFE-E143a	CH_3-O-CF_3	[b,c]3	250
HFE-E227ca1	$CHF_2-O-CF_2CF_3$	[b,e,f]16.05	252
		[b,e,f]33	251
HFE-E236ca1	$CHF_2-O-CF_2CHF_2$	[b,e,f]5.95	252
		[b,e,f]8.5	251
HFE-E236cb1	$CH_2F-O-CF_2CF_3$	[b,e,f]5.9	252
HFE-E227ca2	$CHF_2CF_2-O-CF_3$	[b,e,f]12.1	252
		[b,e,f]17.5	251
HFE-E227ea1	$CF_3CHF-O-CF_3$	[b,c]11	250
		20	258
		[b,e,f]23.5	251
		[b,e,f]14.9	252
HFE-E236cb2	$CH_2FCF_2-O-CF_3$	[b,e,f]6.7	252
HFE-E236ea1	$CHF_2-O-CHFCF_3$	[a]4.04	257
		[b,e,f]6.5	251
		[b,e,f]7.5	252
HFE-E236ea2	$CHF_2CHF-O-CF_3$	[b,e,f]5.1	252
		[b,e,f]4.55	251
HFE-E236mf1	$CF_3CH_2-O-CF_3$	[b,c]3.7	250
		[b,e,f]4.75	252
HFE-E245ca1	$CH_2F-O-CF_2CHF_2$	[b,e,f]3.5	252
HFE-E245ca2	$CHF_2-O-CF_2CH_2F$	[a]2.18	257
		[b,e,f]6.5	251
		[b,e,f]4.4	252
HFE-E245cb1	$CH_3-O-CF_2CF_3$	6.5	256
		[b,c]1.2	250
		[b,e,f]0.85	251
		[b,e,f]1.4	252
HFE-E245ea1	$CHF_2-O-CHFCHF_2$	[b,e,f]2.75	252
HFE-E245eb1	$CH_2F-O-CHFCF_3$	[b,e,f]2.2	252
HFE-E245eb2	$CH_2FCHF-O-CF_3$	[b,e,f]3.35	252
HFE-E254ea1	$CH_2F-O-CHFCHF_2$	[b,e,f]1.3	252

Halocarbon No.	Chemical Formula	Atmospheric Lifetime (years)	Reference
HFE-E254ea2	$CH_2FCHF-O-CHF_2$	[b,e,f]1.75	252
HFE-E254eb1	$CH_3-O-CHFCF_3$	[b,f]0.5	252
HFE-E254ca1	$CH_2F-O-CF_2CH_2F$	[b,e,f]3.1	252
HFE-E245cb2	$CH_3CF_2-O-CF_3$	[b,e,f]11.2	252
		[b,e,f]27.5	251
HFE-E245fa1	$CHF_2-O-CH_2CF_3$	[b,c]5.2	250
		[b,c]1.7	251
		[b,e,f]1.15	251
		[a]4.7	257
		[b,f]1.9	252
HFE-E245fa2	$CF_3-O-CH_2CHF_2$	[c]2.2	251
		[b,e,f]1.45	251
		[b,e,f]2.65	252
HFE-E254cb1	$CH_3-O-CF_2CHF_2$	[a]0.47	257
		[b,c]0.85	251
		[b,e,f]0.35	251
		[b,e,f]0.95	252
HFE-E254cb2	$CH_3CF_2-O-CHF_2$	[b,e,f]3.85	252
		[b,e,f]6	251
HFE-E254eb2	$CH_3CHF-O-CF_3$	[b,e,f]2.45	252
HFE-E254fa1	$CHF_2-O-CH_2CHF_2$	[b,e,f]1.05	252
		[b,e,f]0.45	251
HFE-E356mcf2	$CF_3CH_2-O-CF_2CH_2F$	[a]1.8	257
HFE-E356mec1	$CH_3-O-CF_2CHFCF_3$	[b,c]0.94	251
HFE-E356mff2	$CF_3CH_2-O-CH_2CF_3$	[a]0.5	257
HFE-E356pcc1	$CH_3-O-CF_2CF_2CHF_2$	[b,c]0.93	251
HFE-E356pfc1	$CHF_2-O-CH_2CF_2CHF_2$	[b,c]1.3	251
HFE-E356pfc2	$CHF_2CH_2-O-CF_2CHF_2$	[b,c]2	251
HFE-E365mc1	$CH_3-O-CH_2CF_2CF_3$	[b,c]0.11	251
HFE-E365sf2	$CH_3CH_2-O-CF_2CF_3$	[a]0.3	257
HFE-E374pcf2	$CH_3CH_2-O-CF_2CHF_2$	[b,c]0.43	251
HFE-E4-3-10pccc124	$CHF_2-O-CF_2-O-CF_2CF_2-O-CHF_2$	[b,c]7	249
HFE-E254fb1	$CH_2F-O-CH_2CF_3$	[b,f]0.5	252
HFE-E254fb2	$CH_2FCH_2-O-CF_3$	[b,e,f]1.6	252
		[b,e,f]0.7	251
HFE-E263fb1	$CH_3-O-CH_2CF_3$	[b,c]0.1	251
		[b,f]<0.1	251
		[b,c]0.1	251
HFE-E263fb2	$CH_3CH_2-O-CF_3$	[b,f]0.3	251
HFE-E329p2	$CHF_2CF_2-O-CF_2CF_3$	[b,c]6.8	251
HFE-E338mf2	$CF_3CH_2-O-CF_2CF_3$	[b,c]4.3	251
HFE-E347pf1	$CHF_2-O-CH_2CF_2CF_3$	[a]1.62	257
HFE-E347pf2	$CF_3CF_2-O-CH_2CHF_2$	[b,c]2.8	251
HFE-E347s1	$CH_3-O-CF_2CF_2CF_3$	6.4	241

Halocarbon No.	Chemical Formula	Atmospheric Lifetime (years)	Reference
		^{b,c}1.3	251
		5.6	258
HFE-E449s1	$CF_3CF_2CF_2CF_2$-O-CH_3	4.1	260
HFE-E569sf2	$CF_3CF_2CF_2CF_2$-O-CH_2CH_3	1.2	261

a Estimated
b For reaction with •OH only.
c Non-rigorous calculation.
d See Reference
e Average
f Estimated from HOMO energy.

Extinguishment Testing

1-Methoxynonafluorobutane, HFE-7100, was obtained from 3M Company. Hydrofluoropolyether was obtained as an experimental product from Ausimont S.p.A. in Milano, Italy. As expected and indicated in Table 7–47, neither of these compounds exhibited extinguishment performance suggesting a chemical extinguishment mechanism. The flame extinguishing results are comparable to HFCs.

Table 7–47. Fluoroether Cup Burner Extinguishment Data.

Compound Name	Formula	T_b (°C)	Cup Burner Flame Extinguishment (Volume %)
1-Methoxynonafluorobutane	$CF_3CF_2CF_2CF_2$-O-CH_3	60	6.1
Hydrofluoropolyether	$HF_2CO(CF_2O)_n(CF_2CF_2O)_mCF_2H$	100	5.1

Assessment Summary

There was little reason to pursue hydrofluoroethers or perfluoroethers further. The fire suppression efficiencies were comparable to the HFCs, and the larger molecular weights led to higher boiling points. There was no indication that the ether linkage provided any significant contribution to rainout; the polarity is too small. Perfluorinated saturated ethers were expected to have atmospheric lifetimes similar to those of the perfluorinated alkanes, a property that generally made their use as halon replacements questionable. The atmospheric lifetimes for partially fluorinated ethers were much shorter. The low reactivity of the ether linkage causes ethers to be relatively biologically benign, though there are many exceptions; anesthesia is a problem in some cases.

7.4.8 Bromofluoroethers

Atmospheric Lifetime, ODP, and GWP

The atmospheric lifetimes of bromofluoroethers are expected to be similar to those of the base fluoroether. The only bromofluoroether whose atmospheric lifetime has been studied is Roflurane, CH_3-O-CF_2CFBrH (T_b = 89 °C), a compound once employed as an anesthesia agent.[262] The reported estimate of atmospheric lifetime was 14 days.

Toxicity Assessment Summary

Toxicity data for the bromofluoroethers are scarce. However, Roflurane has been shown to have a very low toxicity.[263] This is a hopeful sign that other members of the bromofluoroether family would be of acceptable toxicity.

Volatility and Availability

The boiling point screening criterion of 20 °C severely limited the number of bromofluoroethers considered. Bromofluoroethers with one or both of the alkyl groups having two or more carbons and with the bromine atom on a carbon atom not adjacent to the ether linkage typically have boiling points above 60 ºC. Thus attention focused on the halogenated dimethyl ethers and a limited number of methyl ethyl ethers. Having at least a one-to-one ratio of fluorine atoms to hydrogen atoms ensured non-flammability.

With variation in site of bromination and fluorination, a large number of structural isomers are possible even with this very limited range of ethers. The number of compounds was reduced through a selection process which focused on the most symmetrically substituted compounds (lower expected boiling point) and those compounds expected to be the least polar based on calculated octanol water partition coefficients. This latter criterion was expected to help select the least toxic compounds (Chapter 6).

Synthesis of the brominated dimethyl ethers was first presented by Adcock and co-workers in 1991.[23] Further clarification and elaboration from Prof. Adcock enabled the successful synthesis of bromodifluoromethyl difluoromethyl ether, CF_2Br-O-CF_2H.[264] This information indicated that elemental bromine did not substitute in these ethers in good yields without decomposition, and that the more reactive interhalogen compound, bromine chloride, should be employed. In this method, equimolar amounts of chlorine and bromine formed bromine chloride during short pre-irradiation of the halogen mixture prior to introduction of the fluorinated ether. While a small excess of bromine suppressed virtually any chlorination, too large an excess of bromine significantly slowed the rate of reaction. Stepwise bromination of the dihydryl fluoroether, HCF_2-O-CF_2H was observed under these conditions. Additional synthetic information provided valuable guidance and enabled the successful synthesis of adequate amounts of CF_2Br-O-CF_2H for very limited extinguishment testing. That guidance included:

- Employ a high pressure Hg lamp. The high pressure lamp gave a pressure broadened spectrum, unlike the older medium pressure or low pressure lamps, and therefore provided an increased rate of reaction. Medium and low pressure lamps did not work in this reaction.
- Eliminate all O_2 and H_2O from the bromine and chlorine reactants and the bisdifluoromethyl ether. Remove all air (O_2 and H_2O) from all glassware and photolysis equipment. These were extremely important steps, and failure of the reaction resulted when they were not followed.
- Adjust the Br_2/Cl_2 ratio such that Br_2 is in very slight excess to Cl_2. The amount of Br_2 employed was approximately stoichiometric to the fluoroether being brominated. This method was reported to require only a couple of hours of photolysis. In the reaction, chlorine abstracted hydrogen and bromine, then added to form the product. When too high a Br_2:halocarbon ratio was employed, the reaction slowed down due to light absorption. When too much chlorine was present, chlorination of the ether occurred instead of the desired bromination.

The reaction is tricky, and several attempts were needed to optimize the synthetic conditions. With recycling of unreacted reactants, a high yield may well be achieved.

Flame Extinguishment

The contribution from the bromine atom was expected to dominate suppression of flame chemistry, with some thermal contributions to flame suppression from the more heavily fluorinated alkyl groups.

Prior to the NGP, only two measurements of flame suppression by the higher boiling hydrobromofluoroethers (HBFEs) had been carried out. $CH_2=CBr(OCF_3)CF_2CF_3$, which is unsaturated, had a cup burner extinguishment concentration of 3.8 volume %.[240] Roflurane, CH_3-O-CF_2CHBrF, was estimated to have a heptane cup burner volume fraction of 4.2 % and a short atmospheric lifetime.[240] Table 7–48 summarizes the NGP cup burner test data for five of the lowest molecular weight compounds in this family. All confirmed the flame extinguishment expectation.

Table 7–48. Bromofluoroether Cup Burner Testing Summary.

Compound Name, Formula	Chemical Formula	T_b (°C)	Cup Burner Extinguishment (volume %)
1-Bromo-1,2,2-trifluoroethyl trifluoromethyl ether	CF_3-O-$CFBrCF_2H$	42	<[c] 4.5
2-Bromo-1,1,2-trifluoroethyl trifluoromethyl ether	CF_3-O-$CHFCF_2Br$	37	< 4.5
Bromomethyl trifluoromethyl ether	CH_2Br-O-CF_3	39	3.2
Bromodifluoromethyl difluoromethyl ether	CF_2Br-O-CF_2H[a]	20-24 (est.)	3.7 (2.4)[b]
Bromomethyl difluoromethyl ether	CH_2Br-O-CF_2H	70	3.6

a Impure sample 65 % bromodifluoromethyl difluoromethyl ether, 25 % bisdifluoromethyl ether, 10 % other ethers
b Estimated extinguishment value based on a 65 % purity
c < signify upper limit extinguishment value.

The cup burner flame extinguishment performance of the sample of 65 volume % bromodifluoromethyl difluoromethyl ether was initially calculated as if the sample were 100 % pure. When the observed 3.7 volume % extinguishment value was corrected for the actual 65 % purity of the sample, an extinguishment value of 2.4 volume % was obtained. It was unlikely that the major impurity in this sample (bisdifluoromethyl ether) contributed significantly to extinguishment at its effective low concentration of 0.9 volume %. The remaining impurities in this sample included predominantly chlorinated analogues to the desired product.

Substituting additional fluorine for a hydrogen on CH_2Br-O-CF_3 might yield a compound (probably a mixture of two structural isomers) with a boiling point in the vicinity of 20 ºC to 30 °C. This might be worthwhile if the low temperature performance requirement were eased (Chapter 2). Bromofluoromethyl trifluoromethyl ether ($CFHBr$-O-CF_3) was also of interest. However, the fluoroether starting material (CFH_2-O-CF_3) was not available. Other possible low boiling chemicals in this family are CF_2Br-O-CH_2F, $CHFBr$-O-CHF_2, CF_2Br-O-CF_3, and CF_2Br-O-CHF_2.

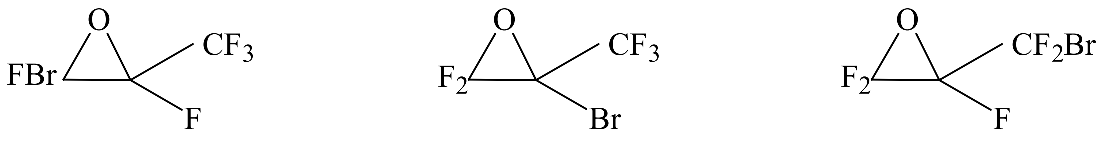
Assessment Summary

There is some potential for the bromofluoroethers as total flooding fire suppressants. While the lowest boiling points are not low enough for effective dispersion under the current operational requirement, there are some structural isomers with boiling points as low as 20 °C to 24 °C. There is reason to expect that some of these compounds might have relatively low toxicity. Limited atmospheric lifetime estimates suggest the possibility of acceptable performance.

7.4.9 Bromofluorooxiranes

The propene oxides (or oxiranes) were expected to be stable, low boiling compounds. As carriers of bromine, there was potential for them to exhibit acceptable flame extinguishment properties as well. Testing indicated that the non-brominated perfluoropropene oxide has a cup burner value of 9.6 volume %.[265] The toxicities of these compounds are unknown. Since they may be readily attached by OH radicals, their atmospheric lifetimes may well be short, but this is unconfirmed.

There are three possible bromine locations in the pentafluorinated propene oxide molecule. Further isomerism due to the formation of one or more optically isomeric carbons results in further isomeric complexity. This complexity yields a total of eight unique compounds, Figure 7–12.



1-Bromopentafluorooxirane (4 optical isomers possible)

2-Bromopentafluorooxirane (2 optical isomers possible)

3-Bromopentafluorooxirane (2 optical isomers possible)

Figure 7–12. Structural and Optical Isomerism of Bromopentafluoropropene Oxide.

Synthesis of 3-bromopentafluorooxirane has been reported.[266] A brief survey of the literature also revealed that 30 % hydrogen peroxide in a basic medium had been used successfully in the epoxidation of fluorinated alkenes such as hexafluoropropene.[267] These compounds might also potentially be synthesized in a single step from existing bromofluoropropenes by a partial oxidation of the alkene bond. $CF_2(O)CBrCF_3$ (2-bromo-1,2-perfluoropropene oxide) was successfully sourced and its flame extinguishment properties determined, as indicated in Table 7–49. Since the cup burner results was higher than generally expected of a brominated compound and since the boiling point was marginal, NGP investigation of the bromofluoropropene oxides was halted.

Table 7–49. Bromofluoropropene Oxide Cup Burner Testing Summary.

Compound Name	T_b (°C)	Cup Burner Extinguishment (volume %)
2-Bromopentafluorooxirane	20 (est.)	4.9
1-Bromopentafluorooxirane	Unknown	Sourced, not acquired
3-Bromopentafluorooxirane	Unknown	Sourced, not acquired

7.4.10 Bromofluoro / Fluorinated Aldehydes and Ketones

Fluorinated Aldehydes and Ketones

An analysis of the potential suitability of fluorinated aldehydes and ketones as halon replacements concluded that further study was warranted.[39] This determination resulted in the “Highly Efficient Thermal Agents” research briefly described earlier in section 7.4.1 of this chapter.[147]

The suitability of fluoroketones was also demonstrated during the course of the NGP by 3M Corporation with their successful commercialization of the perfluoroketone, dodecafluoro-2-methylpentan-3-one, $CF_3CF_2C(O)CF(CF_3)_2$, FK-5-1-12. This compound has a cup burner heptane extinguishment of 4.5 volume %,[268] but a boiling point (49 ºC) well above that required for efficient dispersion under in-flight conditions. Its short atmospheric lifetime yields a lower GWP value than those of the HFCs. Other than the reported data for FK-5-1-12, fire suppression data are almost completely unknown for fluorinated carbonyl compounds.

Bromofluoro Aldehydes and Ketones

2-Bromo-2,2-difluoroethanal, $CBrF_2CHO$, was the sole representative compound that had been studied. The cup burner value for this compound was reported to be 4.4 volume %, and the boiling point was about 40 ºC.[269] As all other examples of bromofluoro aldehydes would likely have higher boiling points, further consideration of this family was not pursued.

7.4.11 Bromofluoro Alcohols

Initial evaluations of bromofluoro alcohols were conducted by the Advanced Agent Working Group, which found that chemical instability of this family was problematic. NGP research identified no additional compounds worthy of study, as the boiling points of the brominated fluoroalcohols were higher than required for in-flight fire suppression (Table 7–50).

It appeared that extinguishment might not be obtainable for alcohols in which the hydrogen content is significant. Thus, better flame extinguishment might be found for compounds such as $CBrF_2CF_2OH$ and CBr_2FCF_2OH. While the alcohols have the advantage of being highly susceptible to “rain out” and would therefore have a lower atmospheric lifetime, they also have boiling points well above those required for aircraft applications and were not pursued further under the NGP.

Table 7–50. Bromofluoro Alcohol Boiling Points.

Compound Formula	T_b (°C)	Cup Burner Flame Extinguishment Value (volume %)	Reference
$CBrF_2CH_2OH$	67 (2 kPa)	did not always extinguish	[270]
$CF_3CHOHCH_2Br$	124	4.1	[271]
$CHBrFCH(OH)CF_3$	124		
$CHFBrCF_2CH_2OH$	149		
$CF_3CBrFCH_2OH$	97		
$CF_3CHBrCH_2OH$	108		
$CF_3CH(OH)CHBrCH_3$	66		
$CF_3CBrFCH(CH_3)OH$	112		
$CF_3CBrFC(CH_3)_2OH$	128		
$CF_3CH(OH)CHBrCH_2CH_3$	94		
$CF_3CH(OH)CBr(CH_3)CH_3$	68		
$CF_3CBrClC(CH_3)_2OH$	137		
$CF_3CBr_2C(CH3)_2OH$	152		
$CF_3CHOHCHBr_2$	155-158	4.78	270
CBr_2FCH_2OH	85 (2.7 kPa)	4.56, appeared flammable	270

7.4.12 Iodinated Hydrocarbons

Iodofluoroalkanes

Nearly all the attention in this family has been directed at CF_3I. CF_3I has a boiling point that is uniquely low (Table 7–51), perhaps low enough for consideration for in-flight applications (although, see Chapter 8). In addition, the iodine atom imparts cup burner flame extinguishment effectiveness to these compounds that is comparable to the bromine atom in halon 1301. When released in the lower atmosphere, the fluorinated iodoalkanes all degrade by photolysis of the carbon–iodine bond and are expected to have short atmospheric lifetimes.[19] These factors led to expectation that CF_3I would be a near drop-in replacement for CF_3Br, which has a cup burner value of 2.9 volume %.

However, experiments revealed unsatisfactory low temperature distribution of CF_3I (Chapter 8 and Reference 272) and raised concerns over its materials compatibility and chemical stability.[273,274,275,276,277] In addition, this compound's LOAEL was measured to be 0.5 volume %,[278,279] resulting in it being deemed unacceptable for use in normally occupied areas.

There have been studies that indicate a reduced cardiac sensitization hazard from an inadvertent release of CF_3I. An early report of experimental discharge modeling of the potential for CF_3I exposure attempted to quantify the potential for aircraft service ground crew exposure to CF_3I during inadvertent agent discharge in one of the engine nacelles during maintenance operations, or pre-take-off inspection.[280] Employing differential IR imaging and sampling of the CF_3I plume, the study's authors provided evidence of a CF_3I plume at the LOAEL concentration and suggested a need for further investigation. Extensive efforts to model human inhalation exposure effects employed a physiologically-based pharmacokinetic (PBPK)[281] approach, described in Chapter 6, that yielded a better understanding of the relationship between exposure concentration and the resulting blood levels following exposure to CF_3I.

Table 7–51. Iodoalkane Boiling Points.

Chemical Formula	T_b (°C)	Cup Burner Flame Extinguishment Value[265] (volume %)
CF_3I	-22.5	3.0
CHF_2I	21.6	
CH_2FI	53.5	
CH_3I	42.5	
C_2F_5I	12	2.1
CHF_2CF_2I	39.4	
C_3F_7I	41.2	3.0
C_4F_9I		2.8
$C_6F_{13}I$		2.5
$C_4F_8I_2$		2.1

One potential application of CF_3I was for inerting aircraft fuel tanks, particularly in the F-16, against in-flight fires and explosions. Considerable controversy arose over this use. As a result, at the request of the Under Secretary of Defense (Acquisition, Technology and Logistics), the Director of Defense Research and Engineering convened an Independent Review Panel (IRP) to assess the four critical technical issues and comment on how they might affect implementation of CF_3I as a viable substitute for halon 1301 in the F-16 inerting application.[282] This assessment of the suitability of CF_3I as a replacement for halon 1301 as an inerting agent in F-16 wing fuel tanks concluded, based on an analysis of materials compatibility, low temperature performance, human toxicology, and atmospheric chemistry, that:

- CF_3I is more chemically reactive than halon 1301. After further qualification testing, it may be possible to specify materials that could be used in service with CF_3I.
- CF_3I is inadequate as a replacement for halon 1301 in the existing F-16 system due to its higher boiling point and resultant reduced delivery pressure at low temperatures.
- CF_3I is more toxic than halon 1301. It would be unwise to replace a chemical with a more toxic one. More rigorous toxicity testing of CF_3I would provide a more quantitative estimate of its toxicity in realistic exposure scenarios.
- Ozone depletion from F-16 application of CF_3I could be as small as ⅛ that of halon 1301 (at lower altitudes) or as large as 1⅔ times as damaging as halon 1301 (at higher altitudes). In any case, CF_3I use onboard an F-16 would be a Class I substance if significant amounts are released above 6,000 m (20,000 ft), and the U.S. Clean Air Act bans use of Class I substances.

This last finding was based on (a) the historical altitudes at which halon 1301 was emitted to the atmosphere following deployment for inerting fuel tanks and (b) the ozone depleting effectiveness of CF_3I. The latter is very sensitive to the altitude of release, since this compound degrades efficiently at low altitudes, but is even more effective than halon 1301 at destroying ozone should it reach the stratosphere following a high altitude release. For fuel tank inerting, the outcome of a detailed analysis was not favorable to the implementation of CF_3I as a halon 1301 replacement.

Since the NGP was responsible for identifying potential candidates for replacing halon 1301 for fire suppression in aircraft engine nacelles, it was important to know whether the different release altitudes for this application might lead to different ozone depletion results. Wuebbles and co-workers at the University of Illinois used a two-dimensional atmospheric model (the 2004 version of the UIUC 2D Chemical Transport Model, CTM) to calculate the effect of CF_3I on stratospheric ozone for this application. For comparison, they re-visited the use of this agent for fuel tank inerting.[283,284]

The 2004 version of the CTM determined the atmospheric distribution of 89 chemically active atmospheric trace constituents with 70 photolytic reactions, 189 thermal reactions, and heterogeneous reactions. Reaction-rate constants and photochemical data in the model were primarily based on the recommendations compiled by the NASA Panel for Data Evaluation.[285,286] The model domain extended from pole to pole and from the ground to 84 km in altitude. A grid box was 5 degrees of latitude and 1.5 km in log-pressure altitude.

The altitude profile of releases of halon 1301 for engine nacelle (and auxiliary power unit) fire suppression was from Bein's compilation of historic data from the military Safety Centers (Chapter 2 and Reference 287). The data encompass over 6,000 incidents from 1980 through 2002. Table 7-51 shows the distribution as inserted into the CTM.

Table 7–52. Compilation of Historic Firefighting Emissions of CF_3Br.

Flight Height (km)	Model Layer	Emission (kg)	Percent of Total Emissions
12 to 13.5	layer 9	8.7	0.57
10.5 to 12	layer 8	13.3	0.87
9 to 10.5	layer 7	77.9	5.07
7.5 to 9	layer 6	22.4	1.46
6 to 7.5	layer 5	142.3	9.26
4.5 to 6	layer 4	45.0	2.93
3 to 4.5	layer 3	61.5	4.00
1.5 to 3	layer 2	115.6	7.52
0 to 1.5	layer 1	1050.0	68.3

Wuebbles and co-workers ran three cases for the latitudes at which the emissions occurred. For 0 °N to 10 °N, the ODP value was 0.084; for 30 °N to 40 °N, the OPD value was 0.028; and for 55 °N to 65 °N, the ODP value was 0.036. All were well below the control value of 0.2 in the U.S. Clean Air Act, but near the cautionary value of 0.05 used by the U.S. Environmental Protection Agency (EPA). In general, since most of CF_3I emissions in this estimate occurred at lower altitudes, they did not tend to deplete atmospheric ozone severely. Therefore, provided this CF_3I emission profile continues to be representative of the actual release characteristics, CF_3I released from aircraft for fighting engine nacelle fires should have a low impact on the ozone layer relative to that of CF_3Br.

In revisiting the effect of replacing CF_3Br with CF_3I for fuel tank inerting, Wuebbles and co-workers used an updated (2004) version of the CTM. They also used two different altitude distributions of suppressant release, thus performing a sensitivity analysis. The first distribution was that used in the original calculations described in Reference 282. The second was an alternative distribution from Van Horn et al.[288] The two are shown graphically in Figure 7-13; the calculated ODP values are shown in Table 7–53.

In the original estimate, the resulting ODPs were in the range of 0.07 to 0.25, mostly below the control value of 0.2 in the U.S. Clean Air Act, but above the EPA value of concern of 0.05. With respect to the Van Horn estimate, all the resulting ODPs were no more than 0.05. Given the fact that aircraft were typically operated at mid-latitudes (the two southern cases calculated here) in the Northern Hemisphere, CF_3I emissions following the Van Horn estimate would not have a substantial impact on ozone.

The model calculations show that the altitude where CF_3I is released from aircraft is a dominant factor in its ozone depletion effects. However, using either distribution, the aircraft-released CF_3I would have much lower impact on the ozone layer than CF_3Br.

These computation estimates are subject to specific uncertainties. Iodine chemistry is not as well understood as that for chlorine and bromine. Heterogeneous reactions between reactive iodine and other active atmospheric reactants on the surface of aerosols could accelerate the ozone destruction rate of iodine catalytic cycles, which could result in much larger ODP values for CF_3I. Extensive studies using a three-dimensional global transport model of the troposphere and stratosphere would enhance confidence in the results from this two-dimensional model.

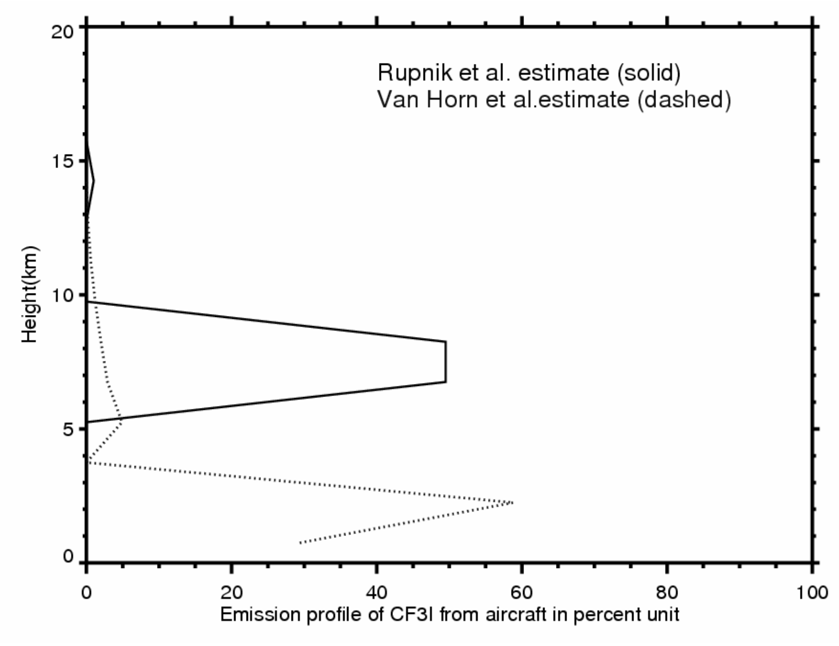


Figure 7-13. Vertical Profiles of CF_3I Emissions for Fuel Tank Inerting in Military Aircraft. Percent unit is mass-weighted.

Table 7–53. Estimated Ozone Depletion Effects of CF_3I for Two Emission Profiles.

Latitude Range	ODP	
	Reference 282 (Rupnik et al.)	Reference 288 (Van Horn et al.)
0 °N to 10 °N	0.254	0.050
30 °N to 40 °N	0.084	0.019
55°N to 65 °N	0.071	0.025

In summary, technical issues with CF_3I remain, as far as aircraft use is concerned. While the ODP contribution is much lower than that of halon 1301, it is still close to being a Class 1 substance, depending on the specific altitudes at which it is deployed. The industrial hygiene issues from maintenance discharge persist. Dispersion is questionable in cases of low temperature nacelle and dry bay use.

Iodofluoroalkenes

A prior estimate of the suitability of iodinated alkenes to perform as halon replacements concluded that further study was warranted.[39] No extinguishment studies have been carried out on any iodoalkene, and the effect of the double bond on extinguishment is unknown. As with bromofluoroalkenes, it is possible that some highly halogenated, lower molecular weight iodoalkenes may be flammable.[289] Examples of some of the simplest iodofluoro ethenes are CF_2=CFI, CFH=CHI, CF_2=CHI, CH_2=CFI, and CFH=CFI,

A review of physical property data indicated that boiling points would likely be much higher than acceptable. For example, CF_2=CFI, expected to be one of the most volatile compounds in this family, has a T_b of 30 °C.[192] The values for partially hydrogenated iodofluoroethenes would be higher. There was a lack of sources for these compounds, along with expectation of chemical instability. These ended consideration of these compounds.

Iodine-containing Ethers

Prior analysis of the suitability of iodinated ethers as potential halon replacements concluded that limited further study was warranted.[39] There were no published data regarding the fire suppression effectiveness of these iodinated derivatives. However, as with brominated compounds, the cup burner values should reflect the presence of the iodine atom and should in the vicinity of 3 volume %.

The lightest iodine-containing ether, iodomethyl methyl ether (iodomethoxymethane) has a relatively high boiling point of 122 °C at 101 kPa.[290] It is expected that due to the higher molecular weight (all compounds must contain at least two carbon atoms and an oxygen atom) and the presence of iodine, all these compounds will have volatilities that are unsuitable for total flood application. This undesirable attribute of these compounds resulted in a decision to direct efforts to more promising areas.

7.5 CHEMICAL FAMILY OPTIONS AND REPLACEMENT ISSUES

7.5.1 Suppressant Criteria and Selection Constraints

In this part of the NGP, researchers built on prior work, assessed the state of knowledge, and greatly extended understanding of fire suppression as well as the potential of both inorganic and organic compounds to serve as halon replacements for suppressing in-flight fires in aircraft. Using the screening criteria discussed in Chapter 6 and listed earlier in this chapter, NGP research appraised a near-universal range of chemistries, focusing on those most likely to provide acceptable replacements. Operationally, these criteria were:

- Cup burner flame extinguishment level measured or estimated to be below 5 volume %. This was to obtain fire suppression and reignition quenching efficiency comparable to halon 1301 and higher than the HFCs. To better this 5 volume % limit, a compound must catalytically suppress combustion or have a high heat capacity.

- Boiling points below about 20 °C. For fluids with slightly higher boiling points, similar fluids were considered to see if there might be a lower boiling member of the chemical family. As discussed in Chapter 8, highly effective dispersion at the lowest in-flight temperatures would require boiling points below -40 °C. However, analysis of the altitudes of historical CF_3Br discharges (Chapter 2) indicated that significantly higher boiling points might well be tolerated. Dispensing the agent as a fine mist might also allow for the use of higher boiling fluids, although establishing a sufficiently high dispensing rate is likely to require more extensive and weighty distribution hardware.
- Inclusion of a chemical feature that rendered the chemical tropodegradable, i.e., likely to have a atmospheric lifetime on the order of a month or less.
- Absence of any toxicological data showing that serious effects on people could occur at a concentration lower than that needed to effect flame extinguishment.

During the nearly two decades of searching for halon alternatives since the signing of the Montreal protocol, there has been a major evolution of the most limiting performance criterion. Initially, there was concern that compounds with halon-like fire suppression efficiency and low ozone depletion contribution would be difficult to find. Later, toxicity became prominent, as several potential alternatives to ozone depleting chemicals performed poorly in cardiotoxicity testing (Chapter 6). For suppressing in-flight fires in aircraft, identifying chemicals that would disperse readily emerged as a principal limiting factor.

The premium on compounds with effective dispersion at low temperatures frequently led to conflict with the other screening criteria. Chemicals with a high heat capacity generally were of high molecular weight and high boiling point. Chemicals with a feature that led to tropospheric reactivity were often polar or were composed of a large number of atoms, both of which typically led to higher boiling points.

Finally, many of the compounds that appeared promising in theory were not available commercially. For some of these, the NGP was able to identify a laboratory that was willing to try to synthesize enough chemical for screening tests. This was not always successful. For still other compounds, the NGP was unable to find any source.

7.5.2 General Conclusions

During the formulation of the NGP and continuing through the research stages, the expectation of identifying a true drop-in replacement for halon 1301 for the suppression of in-flight fires in aircraft was quite low. After appraising thousands of compounds, the NGP was indeed unable to identify such a chemical. The requirement that all the properties of the replacement chemical be so similar to those of halon 1301 as to ensure compatibility with existing weapons platforms was too stringent.

The more realistic objective was to identify chemicals that had promise to perform significantly better than HFC-125. Even that proved difficult:

- No strictly thermally active compounds had a boiling point below -40 °C and a fire suppression efficiency superior to that of HFC-125. As will be seen in Chapter 8, a much higher mass of a higher boiling compound would be needed to compensate for condensation losses on cold surfaces. Even if the temperature requirement were relaxed, as discussed in Chapter 2, there were no strictly thermally active compounds that were deemed worthy of further consideration.

- Only one compound, CF_3CN, with a boiling point of -67 °C, met the strictest volatility criterion. However, it required about 9 volume % to suppress a cup burner flame, about the same as HFC-125.
- A few iodoalkanes had boiling points near 0 °C and extinguished cup burner flames at about 3 volume %. However, it was expected they would be no less toxic than CF_3I.
- There were two other compounds with boiling points near or below 0 °C. Attempts were unsuccessful to synthesize $N(CF_3)_3$ (T_b = -10 °C). CF_2BrCN (T_b = 3 °C) extinguished cup burner flames at less than 4 volume %.
- There were some bromoalkenes with cup burner values about 3 volume % to 4 volume % and with boiling points of 25 °C or slightly above. These temperatures are not likely to lead to effective dispersion at cold temperatures, and two similar compounds had performed poorly in cardiotoxicity testing.

Were the low temperature requirement to be relaxed modestly, $N(CF_3)_3$ and CF_2BrCN would have sufficient volatility. However, for the former, a synthesis path is needed, along with an assessment of whether the nitrogen oxides formed following decomposition pose an ozone threat comparable to halon 1301. For the latter, toxicity and atmospheric lifetime data are lacking. Some bromofluoroalkenes would be eligible if the low temperature requirement were relaxed substantially and toxicity data were developed.

The development of hybrid solid propellant fire extinguishers (Chapter 9) presents an alternative means of dispensing a chemically active fire suppressant. In these devices, the compound is either mixed in with the solid propellant or is added to the high temperature exhaust from the unit. In either mode, the boiling point and toxicity are unimportant. What matters is that the additive be chemically effective at flame suppression, that the chemical species that effects the suppression be present in the exhaust flow, and that the mass of the additive be minimized. The NGP has affirmed or established that effective chemical activity is characteristic of compounds containing P, Br, I, Na, or K atoms. Low mass compounds of some of these atoms have significantly increased the effectiveness of SPFEs (Chapter 9).

7.6 REFERENCES

1. Gann, R.G., ed., *Halogenated Fire Suppressants*, ACS Symposium Series 16, American Chemical Society, Washington, DC, 1975.

2. Sheinson, R.S., "Laboratory Through Full Scale: The U. S. Navy Halon Total Flooding Replacement Program," Chapter 16 in *Halon Replacements: Technology and Science*, ACS Symposium Series 611, Miziolek, A. W., and Tsang, W., Eds., American Chemical Society, Washington, DC, 1995, ISBN 0-8412-3327-6, pp. 175-188.

3. Sheinson, R.S., Hahn, J.E., Geary, K., and Williams, F.W., "Quantification of Physical Fire Suppression of Heptane Pool Fires," *Proceedings of the Chemical land Physical Processes in Combustion Symposium*, Eastern Section Combustion Institute, The Combustion Institute, Pittsburgh, PA, (1977).

4. Sheinson, R.S., Gellene, G.J., Williams, F.W. and Hahn, J.E., "Quantification of Fire Suppressant Action on Liquid Pool Fires," *Proceedings of the Eastern States Combustion Institute*, The Combustion Institute, Pittsburgh, PA, (1978).

5. Sheinson, R.S., Penner-Hahn, J.E., and Indritz, D., "The Physical and Chemical Action of Fire Suppressants," *Fire Safety Journal* **15**, 437, (1989).

6. Sheinson, R.S., Carhart, H.W., Musick, J.K., and Williams, F.W., “Halon Acid Production from Full Scale CF_3Br Pool Fire Suppression Tests,” *Proceedings of the Eastern States Combustion Institute*, The Combustion Institute, Pittsburgh, PA, (1979).

7. Sheinson, R.S., J.K. Musick, and Carhart, H.W., “HF and HBr Production from Full Scale CF_3Br (Halon 1301) Fire Suppression Tests),” *Journal of. Fire & Flammability*, **12**, 229-235, (1981).

8. Floden, J.R., and Tapscott, R.E., “The Quest for Chemical Alternatives to Halon 1211,” *The Military Engineer*, **82(537)**, 13-15, August 1990.

9. Nimitz, J.S., Tapscott, R.E., Skaggs, S.R., and Moore, T.A., *Halocarbons as Halon Replacements: Technology Review and Initiation*, ESL-TR-89-38, Vol. 1 of 5, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida, July 1990.

10. Tapscott, R.E., Dierdorf, D.S., Moore, T.A., and Skaggs, S.R., *Halocarbons as Halon Replacements: Technology Review and Initiation, Halon 1301 Replacements*, ESL-TR-89-38, Vol. 2 of 5, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida, March 1993.

11. Tapscott, R.E., Nimitz, J.S., Walters, E.A., and Arneberg, D.L., *Halocarbons as Halon Replacements: Laboratory Testing of Halon 1211 Replacements*, ESL-TR-89-38, Vol. 3 of 5, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida, March 1993.

12. Dierdorf, D.S., Tapscott, R.E., Skaggs, S.R., and Moore, T.A., *Halocarbons as Halon Replacements: Laboratory Testing of Halon 1301 Replacements*, ESL-TR-89-38, Vol. 4 of 5, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida, March 1993.

13. Tapscott, R.E., and Lee, M.E., *Halocarbons as Halon Replacements: Medium-Scale Testing of Halon 1211 Replacements*, ESL-TR-89-38, Vol. 5 of 5, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida, May 1993.

14. *Radiative Forcing to Climate Change: The 1994 Report of the Scientific Assessment Working Group of IPCC*, Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, UK, 1994.

15. *RIVM Study Assesses HFC Policy Options and Effects*, Global Environmental Change Report, Vol. 7, No. 2, p. 4, 27 January 1995.

16. “Denmark to Propose Phaseout for HFCs,” *Ozone Depletion Today*, 7 November 1996.

17. Skaggs, S.R., and Nimitz, J.S., “Estimating Tropospheric Lifetimes and Ozone-Depletion Potentials of One- and Two-Carbon Hydrofluorocarbons and Hydrochlorofluorocarbons,” *Environmental Science and Technology* **26**, 739-744, 1992.

18. Lifke, J.L., Moore, T.A., and Tapscott, R.E., *Advanced Streaming Agent Development, Volume V: Laboratory-Scale Streaming Tests*, Wright Laboratory (WL/FIVCF) and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, June 1996. NMERI 96/2/32540, Vol. 5 of 5.

19. Moore, T.A., Dierdorf, D.S., Skaggs, S.R., and Tapscott, R.E., *Materials Compatibility and Agent Operational Validation for Halon 1301 Replacement: Phase IV,* Vol. 2, NMERI S.S. 2.32(4), March 1993.

20. Tapscott, R.E., Heinonen, E.W., and Brabson, G.D., *Advanced Agent Identification and Preliminary Assessment*, NMERI 95/15/31883, Wright Laboratory (WL/FIVCF), Tyndall Air Force Base, Florida, April 1996.

21. Pitts, W.M., Nyden, M.R., Gann, R.G., Mallard, G.W., and Tsang, W., *Construction of an Exploratory List of Chemicals to Initiate the Search for Halon Alternatives*, Technical Note 1279, National Institute of Standards and Technology, Gaithersburg, MD, (1990).

22. Gann, R.G., Burgess, S.R., Whisner, K.C., and Reneke, P.A., eds., *Papers from 1991-2006 Halon Options Technical Working Conferences (HOTWC)*, CD-ROM, NIST SP 984-4, National Institute of Standards and Technology, Gaithersburg, MD, (2006).

23. Adcock, J.R., Mathur, S. B, Huang, H.Q, Mukhopadhyay, P., Wang, B., "Fluorinated Ethers – A New Family of Halons," in Gann, R.G., Burgess, S.R., Whisner, K.C., and Reneke, P.A., eds., *Papers from 1991-2006 Halon Options Technical Working Conferences (HOTWC)*, CD-ROM, NIST SP 984-4, National Institute of Standards and Technology, Gaithersburg, MD, (2006).

24. *Technology Development Plan for Alternatives to Ozone-depleting Substances for Weapons Systems Use, Final Report*, Office of the Deputy Secretary of Defense (Science and Technology)/Weapons Systems, September 1998.

25. Grzyll, L.R., and Back, D.D., *Development of Quantitative Structure-Property Relationships for Tropodegradable Halocarbon Fire Suppression Agents*, Final Report, SSG Subtask 3.20, Subcontract S-5000.48, Applied Research Associates, Inc., Tyndall Air Force Base, Florida, Mainstream Engineering Corporation, Rockledge, Florida, March 1997.

26. Bausum, H.T., *QSAR Estimates of Toxicity of Candidate Halon Replacement Compounds*, Health Effects Program, U.S. Army Center for Health Promotion and Preventive Medicine, 10 January, 1997.

27. DEREK, copyright by the President and Fellows of Harvard College and LHASA UK Ltd., (1990-1995).

28. Brittain, A.J., *A Toxicological Assessment of 24 Potential Halon Replacement Agents Using Structural Activity Relationship Analysis*, INM Technical Report (Health & Hygiene) N. 97006, The Institute of Naval Medicine, Alverstoke, GOSPORT, Hants, PO12 2DL.

29. Tapscott, R.E., and Mather, J.D., *Toxicity Assessment of Tropodegradable Halocarbons*, Final Report NMERI 97/4/32930, Center for Global Environmental Technologies, prepared for Wright Laboratories, April 1997.

30. Finch, G.L., Barr, E., Nikula, K., Krone, J., Mather, J.D., *Acute Inhalation Toxicity of Candidate Halon Replacement Compounds in Rats*, Lovelace Respiratory Research Institute, Final Report April 22, 1999.

31 Gladnick, N.L., *AAWG #873, AAWG #903, and AAWG #1116: Bacterial Reverse Mutation Test in Salmonella Typhimurium and Escherichia Coli*, DuPont Pharmaceuticals Company, February 29, 2000.

32 Curry, P.T., *AAWG #873: In vitro Chromosome Aberration Test in Human Peripheral Blood Lymphocytes*, DuPont Pharmaceuticals Company - Stine-Haskell Research Center, November 20, 2000.

33. Horrell, P.J., *Agent 873, An Inhalation Study to Investigate the Cardiac Sensitization Potential in the Beagle Dog.* Huntingdon Life Sciences Limited, Final Report - September 16, 2002.

34. AAWG Minutes reporting results of cardiac sensitization testing of 1-bromo-3,3,3-trifluoropropene, Halon Alternatives Research Corporation, Arlington, VA.

35. Lu, G.G., Ling, J.S.L., and Krantz, J.C., Jr., "Anesthesia. XLI: The Anesthetic Properties of Certain Fluorinated Hydrocarbons and Ethers," *Anesthesiology* **14**, 466-472, (1953).

36. Krantz, J.C., Jr., and Rudo, F.G., "The Fluorinated Anesthetics," in *Handbook of Experimental Pharmacology*, Vol. 20/1, Eichler, O., Farah, A., Herken, H., and Welch, A. D., editors, Springer-Verlag, Berlin, Germany, Chapter 10, pp. 501-564, (1966).

37. Tapscott, R.E., Heinonen, E.W., and Mather, J.D., *Identification and Proof Testing of New Total Flooding Agents: Toxicity and Global Environmental Assessment*, Interim Report, NMERI Report No.

97/29/33010, U. S. Department of Defense, Strategic Environmental Research and Development Program and Defense Advance Research Projects Agency, Arlington, Virginia, February 1998.

38. Tapscott, R.E., Mather, J.D., Heinonen, E.W., Lifke, J.L., and Moore, T.A., *Identification and Proof Testing of New Total Flooding Agents: Combustion Suppression Chemistry and Cup Burner Testing*, Final Report, NMERI Report No. 97/6/33010, U. S. Department of Defense, Strategic Environmental Research and Development Program and Defense Advance Research Projects Agency, Arlington, Virginia, May 1998.

39. Tapscott, R.E., Sheinson, R.S., Babushok, V., Nyden, M.R., and Gann, R.G., *Alternative Fire Suppressant Chemicals: A Research Review with Recommendations*, NIST Technical Note 1443, National Institute of Standards and Technology, Gaithersburg MD, (2001).

40. Patterson, R.A., Gobeli, G.W., Brabson, G.D., and Tapscott, R.E., *Advanced Streaming Agent Development, Volume II: Metal Compounds*, WL-TR-96-XX, NMERI Report No. 96/3/32540, Vol. 2 of 5, Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida, and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, June 1996.

41. Moore, T.A., and Weitz, C.A., *Laboratory Optimization and Medium-Scale Screening of Halide Salts and Water Mixtures*, NMERI Report No. 96/12/32590, U. S. Army Tank-Automotive and Armament Command (TACOM), Warren, Michigan, June 1996.

42. McCamy, C.S., Shoub, H, and Lee, T.G., "Fire Extinguishment by Means of Dry Powder," *Proceedings of the Combustion Institute* **6**, 795-801, (1957).

43. Shen, K.K., and Ferm, D.J., "Boron Compounds as Fire Retardants," *Proceedings, Flame Retardants—101: Basic Dynamics*, Baltimore, Maryland, pp. 137-146, 24-27 March 1996.

44. Kasem, M.A., and Richards, H.R., "Flame-Retardants for Fabrics," *Industrial and Engineering Chemistry, Product Research and Development* **11**, 114-133, (1972).

45. Raether, L.O., "Flame Retardant Markets, Products, Regulations, a Historical Perspective," *Proceedings, Flame Retardants—101: Basic Dynamics*, Baltimore, Maryland, pp. 1-11, 24-27 March 1996.

46. Friedman, R., and Levy, J.B., "Inhibition of Methane-Air Flames by Gaseous Aluminum Chloride," *Combustion and Flame* **2**, 105-107, (1958).

47. Dolan, J.E., and Dempster, P.B., "The Suppression of Methane-Air Ignitions by Fine Powders," *Journal of Applied Chemistry* **5**, 510-517, (1955).

48. Tapscott, R.E., Heinonen, E.W., and Brabson, G.D., *Advanced Agent Identification and Preliminary Assessment*, WL-TR-95-XX, NMERI Report No. 1995/15/31883, Wright Laboratory (WL/FIVCF), Tyndall Air Force Base, Florida, December 1996.

49. Gobeli, G. W., Tapscott, R. E., and Kaizerman, J. A., *Advanced Streaming Agent Development, Volume I: Silicon Compounds*, WL-TR-96-XX, NMERI Report No. 96/1/32540, Vol. 1 of 5, Wright Laboratory (WL/FIVCF), Tyndall Air Force Base, Florida and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, May 1996.

50. Caporiccio, G., "Chemically Reactive Fluorinated Organosilicon Compounds and Their Polymers," U.S. Patent Number 5,041,588, 20 August 1991, assigned to Dow Corning Corporation, Midland, MI.

51. Hastie, J.W., "Chemical Inhibition of Flames," in *High Temperature Vapors*, Academic Press, New York and London, Chapter 5, pp. 332-357, 1975.

52. Ryzhkov, O.T., Azatyan, V. V., Rubtsov, N.M., and Temchin, S.M., "A Kinetic Study of Chain Branching in Dichlorosilane Oxidation," *Kinetics and Catalysis*, Vol. 36, No. 1, pp. 99-102, 1995, and references therein.

53. Metcalfe, E., Feng, Z., Kendrick, D, and Sejourne, S., "Silicon-Based Flame Retardants," *Proceedings, BCC Conference on Flame Retardancy*, Stamford, Connecticut, 2-4 June 1997.

54. Pierce, O.R., and Kim, Y.K., "High-Temperature Fluorosilicone Elastomers," *Applied Polymer Symposium*, No. 22, pp. 103-125, 1973.

55. Languille, P., Vitat, J.C., Guillemont, A.R., and Remond, J.-P., "Liquid Fire Extinguishing Composition," USA, Patent Number 3,879,297, 22 April 1975. Assigned to Rhone-Progil, Paris, France.

56. Kurylo, M.J., Kaye, J.A., Hampson, R.F., and Schmoltner, A.M., *Present State of Knowledge of the Upper Atmosphere 1993: An Assessment Report*, NASA RP-1337, NASA Office of Mission to Planet Earth Science Division, National Aeronautics and Space Administration, Washington, DC, January 1994.

57. "Atmospheric Chemistry: Measurements, Mechanisms and Models: General Discussion," *Faraday Discussions* **100**, 441-457, (1995).

58. Lide, D.R., ed., *CRC Handbook of Chemistry and Physics*, 86th Edition, CRC Press, Inc., Boca Raton, Florida, USA, 2005.

59. Watson, R.T., Prather, M.J., and Kurylo, M.J., *Present State of Knowledge of the Upper Atmosphere 1988: An Assessment Report*, NASA Reference Publication 1208, National Aeronautics and Space Administration, Washington, DC, August 1988.

60. Plane, J.M.C., "The Chemistry of Meteoric Metals in the Earth's Upper Atmosphere," *International Reviews in Physical Chemistry* **10** (1), 55-106, (1991).

61. Plane, J.M.C., and Helmer, M., "Laboratory Studies of the Chemistry of Meteoric Metals," in *Research in Chemical Kinetics*, Vol. 2, Compton, R. G., and Hancock, G., editors, Elsevier Scientific Publishing Company, Amsterdam, pp. 313-367, 1994.

62. Atkinson, R., "Kinetics and Mechanisms of the Gas-Phase Reactions of the Hydroxyl Radical with Organic Compounds," *Journal of Physical and Chemical Reference Data, Monograph No. 1*, American Chemical Society, Washington, DC, and American Institute of Physics, Woodbury, New York, 1989.

63. Atkinson, R., "Gas Phase Tropospheric Chemistry of Organic Compounds," *Journal of Physical and Chemical Reference Data, Monograph No. 2*, American Chemical Society, Washington, DC, and American Institute of Physics, Woodbury, New York, 1994.

64. Fordham, S., ed., *Silicones*, Philosophical Library, Inc., New York, NY, p. 32, 1960.

65. Y. Sawado, T. Akiyama, T. Ueno, K. Kamisako, K. Kuroiwa, and Y. Tarui, "Contributions of Silicon-Hydride Radicals to Hydrogenated Amorphous Silicon Film Formation in Windowless Photochemical Vapor Deposition System," *Japanese Journal of Applied Physics* **33**, 950-955, (1994).

66. Swanson, S.P., Cull, R.A., Bryant, D., and Moore, J., "New Technologies and Cleaning Performance Based on Volatile Methyl Siloxanes," *Proceedings, International Conference on Ozone Protection Technologies*, Washington, DC, 21-23 October 1996.

67. Sax, N.I., and Lewis, R.J., Sr., *Dangerous Properties of Industrial Materials*, Vol. 1-3, Seventh Edition, Van Nostrand Reinhold, New York, 1989.

68. Gage, J.C., "The Subacute Inhalation Toxicity of 109 Industrial Chemicals," *British Journal of Industrial Medicine* **27**, 1-18, (1970).

69. “Significant New Uses of Certain Chemical Substances: Final Rule,” *Federal Register* **63**(41), 393-3441, 22 January 1998.

70. Michl, J., ed., “Silicon Chemistry,” *Chemical Reviews* **95(**5), (1995).

71. Martel, B., and Hiriart, J.M., “Nouveaux Intermediaires α-Halomethylmetalliques Stables: Formation et Stabilite Remarquable D'α-Halomethylsodium et D'α-Halomethylpotassium,” *Tetrahedron Letters* **29**, 2737-2740, (1971).

72. Hiyama, T., Nishide, K., and Obayashi, S., “Practical Synthesis and Polymerization of Trifluorovinylsilanes. A Possible Precursor of Poly(difluoroacetylene),” *Chemistry Letters*, 1765-1768, 1984.

73. Froberger, C.F., “Synthesis of Tetra(perfluoroalkoxy)silanes,” *Journal of Organic Chemistry* **25**, 311-312, (1960).

74. Morrison, M.E., and Scheller, K., “The Effect of Burning Velocity Inhibitors on the Ignition of Hydrocarbon-Oxygen-Nitrogen Mixtures,” *Combustion and Flame* **18**, 3-12, (1972).

75. Vanpee, M., and Shirodkar, P.P., “A Study of Flame Inhibition by Metal Compounds,” *Proceedings of the Combustion Institute* **17**, 787-795, (1978).

76. Bulewicz, E.M., and Padley, P.J., “Catalytic Effect of Metal Additives on Free Radical Recombination Rates in H_2+O_2+N_2 Flames,” *Proceedings of the Combustion Institute* **13**, 73-80, (1971).

77. Linteris, G. T., “Suppression of Cup Burner Diffusion Flames by Super-Effective Chemical Inhibitors and Inert Compounds,” 2001, in *Papers from 1991-2006 Halon Options Technical Working Conferences (HOTWC)*, CD-ROM, NIST SP 984-4, National Institute of Standards and Technology, Gaithersburg, MD, (2006).

78. Bulewicz, E.M., and Sugden, T.M., “Flame Photometric Studies of Reactions Induced by Nitric Oxide in Hydrogen-Oxygen-Nitrogen Flames I. The Catalyzed Recombination of Atomic Hydrogen and Hydroxyl Radicals,” *Proceedings of the Royal Society of London, Section A* **277**, 143-154, (1964).

79. Babushok, V., Tsang, W., Linteris, G.T., and Reinelt, D., “Chemical Limits to Flame Inhibition,” *Combustion and Flame* **115**, 551-560, (1998).

80. Allen, C.W., “The Use of Phosphazenes as Fire Resistant Materials,” *Journal of Fire Sciences* **11**, 320-328, (1993).

81. Kobayashi, E., “Flame Retarder in Phosphorus Chemistry—Focusing On Phosphazen Derivative,” *Kinozairyo* **4**, 60-71, (1989).

82. Lyons, J.W., *The Chemistry and Use of Fire Retardants*, Wiley-Interscience, New York, (1970).

83. Levchik, S.V., “Mechanistic Studies of Fire Retardancy in Aliphatic Nylons,” *Proceedings, BCC Conference on Flame Retardancy*, Stamford, Connecticut, 2-4 June 1997.

84. Green, J., “Phosphorus-Bromine Flame Retardant Synergy in a Polycarbonate/Polyethylene Terephthalate Blend,” *Journal of Fire Sciences* **12**, 257-267, (1994).

85. Green, J., “A Phosphorus-Bromine Flame Retardant for Engineering Thermoplastics—A Review,” *Journal of Fire Sciences* **12**, 388-408, (1994).

86. Avondo, G., Vovelle, C., and Delbourgo, R., “The Role of Phosphorus and Bromine in Flame Retardancy,” *Combustion and Flame* **31**, 7-16, (1978).

87. Howell, B.A., Uhl, F.M., Liu, C., and Johnston, K.F., "Highly Halogenated Phosphorus-Containing Compounds as Potential Flame Retardant Agents," *Proceedings, BCC Conference on Flame Retardancy*, Stamford, Connecticut, 2-4 June 1997.

88. Bright, D.A., Dashevsky, S., Moy, P.Y., and Williams, B., "Resorcinol bis(diphenyl phosphate), a Non-Halogen Flame-Retardant Additive," *Proceedings, BCC Conference on Flame Retardancy*, Stamford, Connecticut, 2-4 June 1997.

89. Babcock, L.M., Bard, J.K., Leibfried, R.T., "Flame-Retardant Organoxilicon Polymers, Their Manufacture and Articles Produced from Them, European Patent Application EP 556844, 1993, assigned to Hercules (*Chemical Abstracts* 136160f, **120**, 1994).

90. Weil, E.D., and Kim., H.K., "Flame Retardant Unsaturated Resins—An Overview and New Developments," *Proceedings, BCC Conference on Flame Retardancy*, Stamford, Connecticut, 2-4 June 1997.

91. Ebdon, J.R., Joseph, P., Hunt, B.J., Price, D., Milnes, G.J., and Gao, F, "Flame Retardance in Styrenic and Acrylic Polymers with Covalently-Bound Phosphorus-Containing Groups," *Proceedings, BCC Conference on Flame Retardancy*, Stamford, Connecticut, 2-4 June 1997.

92. "Phosphorus Chemistry," *Chemical Reviews* **94**(5), (1994).

93. Kaizerman, J. A., and Tapscott, R. E., *Advanced Streaming Agent Development, Volume III: Phosphorus Compounds*, Vol. 3 of 5," NMERI 96/5/32540, Wright Laboratory (WL/FIVCF) and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, May 1996.

94. Zhivukhin, S.M., Tolstoguzov, V.B., Kireev, V.V., and Kuznetsova, K.G., "Preparation of Chlorophosphazenes," *Russian Journal of Inorganic Chemistry* **10**, 178-180, (1965).

95. Lund, L.G., Paddock, N.L., Proctor, J.E., and Searle, H.T., "Phosphonitrilic Derivatives. Part I. The Preparation of Cyclic and Linear Phosphonitrilic Chlorides," *Journal of the Chemical Society*, 2542-2547, (1960).

96. Sowerby, D.B., "Cyclic Inorganic Compounds. Part I. Chlorine Exchange Reactions with the Chlorophosphonitriles," *Journal of the Chemical Society*, 1396-1400, (1965).

97. Green, B., and Sowerby, D.B., "Fluorination of Aminochlorotriphosphonitriles and the Preparation of Non-geminal Chlorofluorotriphosphonitriles," *Chemical Communications*, 628, (1969).

98. Green, B., and Sowerby, D.B., "Cyclic Inorganic Compounds. Part IX. Fluorination of Bisdimethylaminotetrachlorophosphonitrile," *Journal of the Chemical Society (A)*, 987-991, (1970).

99. John, K., and Moeller, T., "Phosphonitrilic Bromides," *Journal of Inorganic and Nuclear Chemistry* **22**, 199-204, (1961).

100. Walsh, E.J., Derby, E., and Smegal, J., "Nucleophilic Substitutions on Hexachlorocyclotriphosphazene Using 18-Crown-6 Ether Complexes," *Inorganica Chimica Acta* **16**, 9-10, (1976).

101. Steger, E., and Klemm, D., "Beitrag zur Kenntnis von Fluoro-Bromo-Cyclotriphosphaz-enen," *Journal of Inorganic and Nuclear Chemistry* **29**, 1812-1813, (1967).

102. Ranganathan, T.N., Todd, S.M., and Paddock, N.L., "Reaction of Octafluorocyclotetraphosphonitrile with Methyllithium," *Inorganic Chemistry* **12**, 316-323, (1973).

103. Paddock, N.L., Ranganathan, T.N., and Todd, S.M., "Reaction of Methyl-lithium with Phosphonitrilic Fluorides: A Novel Orientation Pattern," *Canadian Journal of Chemistry* **49**, 164-165, (1971).

104. Ramachandran, K., and Allen, C.W., "Organophosphazenes. 15. Reactions of Hexafluorocyclotriphosphazene with *tert*- and *n*-Butyllithium Reagents," *Journal of the American Chemical Society* **104**, 2396-2399, (1982).

105. Moeller, T., Failli, A., and Tsang, F.Y., "Observations on the Butylation of Trimeric and Tetrameric Phosphonitrilic Fluorides," *Inorganic Nuclear Chemistry Letters* **1**, 49-52, (1965).

106. DuPont, J.G., and Allen, C.W., "Organo-Substituted Phosphazenes. 10. Reactions of Hexafluorocyclotriphosphazene with Propenyllithium Reagents," *Inorganic Chemistry* **17**, 393-3096, (1978)

107. Schmutzler, R., "Chemistry and Stereochemistry of Fluorophosphoranes," *Angewandte Chemie International Edition* **4**, 496-508, (1965).

108. Schmutzler, R., "Fluorophosphoranes," *Inorganic Syntheses* **9**, 63-73, (1968).

109. Boodaghians, R.B., Canosa-Mas, C.E., Carpenter, P.J., and Wayne, R.P., "The Reactions of NO3 with OH and H," *Journal of the Chemical Society, Faraday Transactions 2* **84**, 931-948, (1988).

110. Rowland, F.S., "Statospheric Ozone Depletion," in *Annual Review of Physical Chemistry*, Vol. 42, Strauss, H. L., Babcock, G. T., and Leone, S. R., editors, Annual Reviews, Inc., Palo Alto, California, pp. 731-766, (1991).

111. Chase, M.W., Davies, C.A., Downey, J.R., Frurip, D.J., McDonald, R.A., and Syverud, A.N., *JANAF Thermochemical Tables*, 3rd Edition, *Journal of Physical and Chemical Reference Data*, **14**, Supplement 1, (1985).

112. Stedman, D.H., and Fraser, M.E., "Spectroscopy and Mechanism of Chemiluminescent Reaction Between Group V Hydrides and Ozone," *Journal of the Chemical Society, Faraday Transactions 1* **79**, 527-542, (1983).

113. McElroy, M.B., Salwitch, R.J., Wofsy, S.C., and Logan, J.A., "Reductions of Antarctic Ozone Due to Synergistic Interactions of Chlorine and Bromine," *Nature* **321**, 759-762, (1986).

114. Boville, B.W., "Environmental Aspects of Stratospheric Ozone Depletion," UNEP Ozone Meeting, Washington, DC, March 1977.

115. Wofsy, S.C., "Temporal and Latitudinal Variations of Stratospheric Trace Gases: A Critical Comparison Between Theory and Experiment," *Journal of Geophysical Research* **83**, 364-378, (1978).

116. Anderson, J.G., "The Absolute Concentration of O(^{3}P) in the Earth's Stratosphere," *Geophysical Research Letters* **2**, 231-234, (1975).

117. Atkinson, R., "Kinetics and Mechanisms of the Gas-Phase Reactions of the Hydroxyl Radical with Organic Compounds," *Journal of Physical and Chemical Reference Data, Monograph No. 1*, American Chemical Society, Washington, DC, and American Institute of Physics, Woodbury, New York, 1989.

118. Heicklen, J., "The Correlation of Rate Coefficients for H-Atom Abstraction by HO Radicals with C-H Bond Dissociation Enthalpies," *International Journal of Chemical Kinetics* **13**, 651-665, (1981).

119. Atkinson, R., "Estimations of OH Radical Rate Constants from H-Atom Abstraction from C-H and O-H Bonds Over the Temperature Range 250-1000 K," *International Journal of Chemical Kinetics* **18**, 555-568, (1986).

120. Tuazon, E.C., Atkinson, R., Aschmann, S.M., Arey, J., Winer, A.M., and Pitts, J.N., Jr., "Atmospheric Loss Processes of 1,2-Dibromo-3-Chloropropane and Trimethyl Phosphate," *Environmental Science and Technology* **20**, 1043-1046, (1986).

121. Atkinson, R., "Gas Phase Tropospheric Chemistry of Organic Compounds," *Journal of Physical and Chemical Reference Data, Monograph No. 2*, American Chemical Society, Washington, DC, and American Institute of Physics, Woodbury, New York, 1994.

122. Wolfe, R.E., Ellis, D.H., Leahy, H.F., Vinegar, A., and Sharma, S., *Acute Oral Toxicity Evaluation and Genotoxicity Testing of Hexakis(2,2,2-trifluoroethoxy)cyclotri-phosphazene, a Replacement Candidate for Ozone Depleting Substances*, AL/ OE-TR-1997-0054, Armstrong Laboratory, Occupational and Environmental Health Directorate, Toxicology Division, Human Health Systems Center, Air Force Materiel Command, Wright-Patterson AFB, Ohio, ManTech - GEO-CENTERS Joint Venture, Toxic Hazards Research, Dayton, Ohio, May 1997.

123. Weir, P., *Activity of 3899-A Chlorophosphazene in in vitro Mammalian Cell Transformation Assay*, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, October 1978.

124. Weir, P., *Activity of 3899-B Chlorophosphazene in in vitro Mammalian Cell Transformation Assay*, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, October 1978.

125. Weir, P., *Activity of T1352A in in vitro Mammalian Cell Transformation Assay in the Presence of Exogenous Metabolic Activation*, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, March 1979.

126. Weir, P., *Activity of T1356A in in vitro Mammalian Cell Transformation Assay in the Presence of Exogenous Metabolic Activation*, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, March 1979.

127. Weir, P., *Activity of T1350 in the in vivo Cytogenetic Assay in Rodents for Mutagenicity*, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, 1979.

128. Weir, P., *Activity of T1355 in the in vivo Cytogenetic Assay in Rodents for Mutagenicity*, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, 1979.

129. Weir, P., *Activity of T1351A in in vitro Mammalian Cell Point Mutation Assay in the Presence of Exogenous Metabolic Activation*, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, March 1979.

130. Weir, P., *Activity of T1357A in in vitro Mammalian Cell Point Mutation Assay in the Presence of Exogenous Metabolic Activation*, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, March 1979.

131. Weir, P., *Activity of 3899-A-CPP in the Salmonella/Microsomal Assay for Bacterial Mutagenicity*, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, October 1978.

132. Weir, P., *Activity of 3899-B-CPP in the Salmonella/Microsomal Assay for Bacterial Mutagenicity*, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, October 1978.

133. Weir, P., *Activity of 3899-A Chlorophosphazene in a Test for Differential Inhibition of Repair Deficient and Repair Competent Strains of Escherichia Coli: DNA Repair*, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, September 1978.

134. Weir, P., *Activity of 3899-B Chlorophosphazene in a Test for Differential Inhibition of Repair Deficient and Repair Competent Strains of Escherichia Coli: DNA Repair*, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, September 1978.

135. Weir, P., *Activity of T1349 in the Dominant Lethal Assay in Rodents for Mutagenicity*, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, January 1979.

136. Weir, P., *Activity of T1354 in the Dominant Lethal Assay in Rodents for Mutagenicity*, Ethyl Corporation, Baton Rouge, Louisiana, Microbiological Associates, Bethesda, Maryland, January 1979.

137. Gage, J.C., "The Subacute Inhalation Toxicity of 109 Industrial Chemicals," *British Journal of Industrial Medicine* **27**, 1-18, (1970).

138. Sweet, D.V., ed., *Registry of Toxic Effects of Chemical Substances*, Report Number DHHS (NIOSH) 87-114, Vols. 1-5, U. S. Department of Health and Human Services, National Institute for Occupational Safety and Health, Washington, DC, April 1987.

139. Haaland, P.D., and Huntington, J.H., *Halon Replacement for Aircraft Fire Suppression Systems*, Final Report - AFRL-ML-WP-TR-1998-4120, June 1998.

140. Eclipse Aviation press release, August 2005.

141. Lawless, E.W., and Harman, L.D., "Bis(trifluoromethyl)sulfide," *Journal of Inorganic and Nuclear Chemistry* **31**, 1541-1542, (1969).

142. Haas, A., and Oh, D.Y., "Perhalogenierte Sulfenylcarboxylate," *Chemische Berichte* **102**, 77-82, (1969).

143. Sauer, D.T., and Shreeve, J.M., "Bis(Perfluoroalkyl)Sulfur Difluorides and Bis(Perfluoroalkyl)Sulfoxides," *Journal of Fluorine Chemistry* **1**, 1-11, (1971/72).

144. Sauer, D.T., and Shreeve, J.M., "Bis(perfluoroalkyl)sulphur Difluorides and Bis(perfluoroalkyl) Sulphoxides," *Chemical Communications*, 1679-1680, (1970).

145. Lawless, E.W., "Perfluorodimethyl Sulfoxide and Bis(trifluoromethyl)sulfur Difluoride," *Inorganic Chemistry* **9**, 2796-2798, (1970).

146. Krespan, C.G., "Fluorocarbon Metalloid Compounds of Tetrafluoroethylene and Sulfur, Selenium, or Phosphorus and Their Preparation," U.S. Patent 2,931,803, 5 April 1960, assigned to E.I. du Pont de Nemours and Company, Wilmington, DE.

147. Pitts, W.M., Yang, J.C., Bryant , R.A., Blevins, L. G., and Huber, M.L., *Characteristics and Identification of Super Effective Fire Extinguishing Agents, Final Report, NGP project 4C/1*, NIST Technical Note 1440, National Institute of Standards and Technology, Gaithersburg, MD, 2006..

148. Pitts, W.M. and Blevins, L.G., "An Investigation of Extinguishment by Thermal Agents Using Detailed Chemical Kinetic Modeling of Opposed Jet Diffusion Flames," pp. 215-249, Fifteenth Meeting of the UJNR Panel on Fire Research and Safety, NISTIR 6588, National Institute of Standards and Technology, Gaithersburg, MD, (2000).

149. Pitts, W.M. and Blevins, L.G., "An Investigation of Extinguishment by Thermal Agents Using Detailed Chemical Modeling of Opposed Flow Diffusion Flames," 1999, in Gann, R.G., Burgess, S.R., Whisner, K.C., and Reneke, P.A., eds., *Papers from 1991-2006 Halon Options Technical Working Conferences (HOTWC)*, CD-ROM, NIST SP 984-4, National Institute of Standards and Technology, Gaithersburg, MD, (2006).

150. Pitts, W.M. and Blevins, L.G., "An Investigation of Extinguishment by Thermal Agents Using Detailed Chemical Kinetic Modeling of Opposed Flow Diffusion Flames," *Proceedings of the Fall Technical Meeting of the Eastern Section of the Combustion Institute*, pp. 184-187, The Combustion Institute, Pittsburgh, PA, (1999).

151. Yang, J.C., Bryant, R.A., Huber, ML., and Pitts, W.M., "Experimental Investigation of Extinguishment of Laminar Diffusion Flames by Thermal Agents," 2000, in Gann, R.G., Burgess, S.R., Whisner, K.C., and Reneke, P.A., eds., *Papers from 1991-2006 Halon Options Technical Working Conferences (HOTWC)*, CD-ROM, NIST SP 984-4, National Institute of Standards and Technology, Gaithersburg, MD, (2006).

152. Pitts, W.M. and Blevins, L.G., "An Investigation of Extinguishment by Thermal Agents Using Detailed Kinetic Modeling of Opposed Jet Diffusion Flames," Work in Progress Poster 1-K10, Presented at the Twenty-Eight Symposium (International) on Combustion, Edinburgh, Scotland, July 31-August 4, 2000.

153. Pitts, W.M., Bryant, R.A., and Yang, J.C., "Thermal Agent Extinguishment of Two Types of Diffusion Flames," *Proceedings of the Second Joint Meeting of the United States Sections*, The Combustion Institute, Pittsburgh, PA, 2001.

154. Pitts, W.M., Yang, J.C., and Bryant, R.A., "Fuel Effects on the Extinguishment of Laminar Diffusion Flames by Thermal Agents," 2001, in Gann, R.G., Burgess, S.R., Whisner, K.C., and Reneke, P.A., eds., *Papers from 1991-2006 Halon Options Technical Working Conferences (HOTWC)*, CD-ROM, NIST SP 984-4, National Institute of Standards and Technology, Gaithersburg, MD, (2006).

155. Heathfield, A.E., Anastasi, C., Pagsberg, P., and McCulloch, A., "Atmospheric Lifetimes of Selected Fluorinated Ether Compounds," *Atmospheric Environment* **32**, 711-717 (1998).

156. Grzyll, L. R., Back, D. D., Ramos, C., and Samad, N.A., *Development of a Rapid Screening Technique for Second-Generation Halon Alternatives*, SBIR Phase II Final Report, Contract Number DAAH01-93-C-R150, (1996).

157. Minor, B., "Compositions Including a Three Carbon Cyclic Fluoroether," U.S. Patent No. 5480572 (1996).

158. Minor, B., "Compositions Including a Fluoroamine and a Second Component," U.S. Patent No. 5441659 (1995).

159. Minor, B., Chisolm, T. E. C., and Shealy, G. S., "Azeotrope (Like) Compositions with Fluoromethyl Trifluoromethyl Ether and Dimethyl Ether," U.S. Patent No, 5607616 (1997).

160. Sekiya, A. and Misaki, S., "A Continuing Search for New Refrigerants," *Chemtech* **26**, 44-48 (1996).

161. Chueh, C.F. and Swanson, A.C., "Estimation of Liquid Heat Capacity," *Canadian Journal of Chemistry* **51**, 596-600, (1973).

162. Church, C.F., and Swanson, A.C., "Estimating Liquid Heat Capacity," *Chemical Engineering Progress* **69**, 83-85. (1973).

163. Fishtine, S.H., "Reliable Latent Heats of Vaporization," *Industrial and Engineering Chemistry* **55(4)**, 20-28 (1963).

164**.** Rihani, D.N. and Doraiswamy, L.K., **"**Estimation of Heat Capacity of Organic Compounds from Group Contributions," *Industrial and Engineering Chemistry Fundamentals* **4**, 17-21 (1965).

165. Hawley, G.G., *Condensed Chemical Dictionary*, Eighth Ed., Van Nostrand Reinhold Company, New York (1971).

166. 3M Corporation; web site http://www.mmm.com/fluids/7100.html.

167. Salvi-Narkhede, M., Adcock, J.L., Gakh, A., and Van Hook, W.A., "Vapor Pressures, Liquid Molar Volumes, Vapor Non-ideality, and Critical Properties of $CF_3OCF_2CF_2CF_3$, *c*-$CF_2CF_2CF_2CF_2O$, $CF_3OCF_2OCF_3$, and $CF_3OCF_2CF_2H$**,"** *Journal of Chemical Thermodynamics* **25**, 643-647 (1993).

168. Wang, B.H., Adcock, J.L., Mathur, S.B., and Van Hook, W.A., "Vapor Pressures, Liquid Molar Volumes, Vapor Non-Idealities, and Critical Properties of Some Fluorinated Ethers: $CF_3OCF_2OCF_3$, $CF_3OCF_2CF_2H$, *c*-$CF_2CF_2CF_2O$, CF_3OCF_2H, and CF_3OCH_3; and of CCl_3F and CF_2ClH, *Journal of Chemical Thermodynamics* **3**, 699-710 (1991).

169. Matsuo, S., Tanaka, Y., Takada, N., Yamamoto, H., and Sekiya, A., "Gaseous Thermal Conductivities of Fluorinated Methyl Ethyl Ethers," *Journal of Chemical and Engineering Data* **43**, 473-476 (1998).

170. Apollo Scientific, Derbyshire, UK; http://www.apolloscientific.co.uk/.

171. Hamins, A., Gmurczyk, G., Grosshandler, W., Rehwoldt, R. G., Vazquez, I., Cleary, T., Presser, C., and Seshadri, K., "4. Flame Suppression Effectiveness," in *Evaluation of Alternative In-Flight Fire Suppressants for Full-Scale Testing in Simulated Aircraft Engine Nacelles and Dry Bays*, Grosshandler, W. L., Gann, R.G., and Pitts, W.M., eds., NIST SP 861, pp. 345-465, National Institute of Standards and Technology, Gaithersburg, MD (April, 1994).

172. Lutz, A.E., Kee, R.J., Grcar, J.F., and Rupley, F.M., *OPPDIF: A Fortran Program for Computing Opposed-Flow Diffusion Flames*, SAND96-8243, Sandia National Laboratories, Livermore, CA (1996).

173. Kee, R.J., Rupley, F.M., Meeks, E., and Miller, J.A., *CHEMKIN-III: A FORTRAN Chemical Kinetics Package for the Analysis of Gas-Phase Chemical and Plasma Kinetics*, SAND96-8216, Sandia National Laboratories, Livermore, CA (1996).

174. Frenklach, M., Wang, H., Yu, C.-L., Goldenberg, M., Bowman, C.T., Hanson, R.K., Davidson, D.F., Chang, E.J., Smith, G.P., Golden, D.M., Gardiner, W.C., and Lissianski, V., *GRI-MECH 1.2*, http://www.me.berkeley.edu/gri_mech/.

175. Babushok, V. and Tsang, W., "Inhibitor Rankings for Alkane Combustion," *Combustion and Flame* **123**, 488-506 (2000).

176. Ishizuka, S., and Tsuji, H., "An Experimental Study o the effect of Inert Gases on extinction of laminar Diffusion Flames," *Proceedings of the Combustion Institute* **18**, 695-703m (1981).

177. Puri, I., and Seshadri, K., "Extinction of Diffusion Flames Burning Diluted Methane and Diluted Propane in Diluted Air," *Combustion and Flame* **65**, 137-150 (1986).

178. Hamins, A. Building and Fire Research Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, private communication.

179. Simmons, R.F., and Wolfhard, H.G., "The Influence of Methyl Bromide on Flames, Part 1 – Pre-Mixed Flames," *Combustion and Flame* **1**, 155-161 (1957).

180. Babb, M., Gollahalli, S.R., and Sliepcevich, C.M., "Extinguishment of Liquid Heptane and Gaseous Propane Diffusion Flames," *Journal of Propulsion and Power* **15**, 260-265 (1999).

181. Ural, E.A., "Measurements of the Extinguishing Concentrations of Gaseous Fuels Using the Cup Burner Apparatus," in Gann, R.G., Burgess, S.R., Whisner, K.C., and Reneke, P.A., eds., *Papers from 1991-2006 Halon Options Technical Working Conferences (HOTWC)*, CD-ROM, NIST SP 984-4, National Institute of Standards and Technology, Gaithersburg, MD, (2006).

182. Noto, T., Babushok, V.I., Burgess, D.R.F., Hamins, A., Tsang, W., and Miziolek, A., "Effect of Halogenated Flame Inhibitors on C_1-C_2 Organic Flames," *Proceedings of the Combustion Institute* **26**, 1377-1383, 1996.

183. Linteris, G.T., Burgess, Jr., D.R., Babushok, V., Zachariah, M., Tsang, W., and Westmoreland, P., “Inhibition of Premixed Methane–Air Flames by Fluoroethanes and Fluoropropanes,” *Combustion and Flame* **113**, 164-180 (1998).

184. Saso, Y., Zhu, D.L., Wang, H., Law, C.K., and Saito, N., “Laminar Burning Velocities of Trifluoromethane–Methane Mixtures: Experiment and Numerical Simulation,” *Combustion and Flame*.**114**, 457-468 (1998).

185. Papas, P., Fleming, J.W., and Sheinson, R.S., “Extinction of Non-premixed Methane- and Propane-air Counterflow Flames Inhibited with CF_4, CF_3H, and CF_3Br,” *Proceedings of the Combustion Institute* **26**, 1405-1411, 1996.

186. Moore, T.A., Weitz, C.A., and Tapscott, R.E., “An Update of NMERI Cup Burner Test Results,” 1996, in Gann, R.G., Burgess, S.R., Whisner, K.C., and Reneke, P.A., eds., *Papers from 1991-2006 Halon Options Technical Working Conferences (HOTWC)*, CD-ROM, NIST SP 984-4, National Institute of Standards and Technology, Gaithersburg, MD, (2006).

187. Tapscott, R.E., New Mexico Engineering Research Institute, unpublished data, 1997.

188. Flynn, R.M. and Thomas, S.D., “Fire Extinguishing Process and Composition,” U. S. Patent 5,718,293, February 17, 1998.

189. Cohen, N., *Structure-Reactivity Relationships for Predicting Environmentally Hazardous Chemicals*, EPA/600/3-86/072, Environmental Protection Agency, Office of Research and Development, Research Triangle Park, North Carolina, prepared by the Aerospace Corporation, El Segundo, California, December 1986.

190. Prinn, R., Weiss, R.F., Miller, B.R., Huang, J., Alyea, F.N., Cunnold, D.M., Fraser, P.J., Hartley, D.E., and Simmonds, P.G., “Atmospheric Trends and Lifetime of CH_3CCl_3 and Global OH Concentrations,” *Science*, **269 (**5221), 187-192, (1995).

191. Wuebbles, D.J., and Connell, P.S., *A Screening Methodology for Assessing the Potential Impact of Surface Releases of Chlorinated Halocarbons on Stratospheric Ozone*, UCID-19233, Lawrence Livermore Laboratory, Livermore, California, November 1981.

192. SynQuest Laboratories, Inc. online catalog, http//www.synquestlaboratories.com.

193. Huie, R.E., Orkin, V.L., Louis, F.L., Kozlov, S.N., Kurylo, M.J., “Effect of Bromine Substitution on the Lifetimes and Ozone Depletion Potentials of Organic Compounds,” 2002, in Gann, R.G., Burgess, S.R., Whisner, K.C., and Reneke, P.A., eds., *Papers from 1991-2006 Halon Options Technical Working Conferences (HOTWC)*, CD-ROM, NIST SP 984-4, National Institute of Standards and Technology, Gaithersburg, MD, (2006).

194. Tapscott, R.E., and Mather, J.D., “Tropodegradable Fluorocarbon Replacements for Ozone Depleting and Global Warming Chemicals,” *Proceedings of the International Conference on Fluorine Chemistry '99*, Tokyo, (1999).

195. Tapscott, R.E., Mather, J.D., “Tropodegradable Fluorocarbon Replacements for Ozone Depleting and Global Warming Chemicals,” *Journal of Fluorine Chemistry* **101**, 209-213 (2000).

196. Lifke, J., Martinez, A., Tapscott, R.E., and Mather, J.D., *Tropodegradable Bromocarbon Extinguishants*, Final Report to the Strategic Environmental Research and Development Program, Report 99/8/33350, New Mexico Engineering Research Institute, Albuquerque NM, 2001.

197. Ibiricu, M.M., and Gaydon, A.G., “Spectroscopic Studies of the Effect of Inhibitors on Counterflow Diffusion Flames,” *Combustion and Flame* **8**, 51-62, (1964).

198. Hastie, J.W., “Chemical Inhibition of Flames,” in *High Temperature Vapors*, Academic Press, New York and London, Chapter 5, pp. 332-357, 1975.

199. Song, C.E., Kim, I.O., Lee, J.K., Kim, T.K., and Lee, S.G., “Liquid Fire Extinguishing Composition,” USA, Patent Number 5,219,474, 15 June 1993. Assigned to Korea Institute of Science and Technology, Seoul, Republic of Korea.

200. Weil, E.D., and Marolewski, T.A., “A Review of Phosphate Ester Fire Resistance Mechanisms and Their Relevance to Fluid Testing,” in *Fire Resistance of Industrial Fluids,* ASTM STP 1284, Totten, G.E., and Reichel, J., eds., American Society for Testing and Materials (ASTM), Philadelphia, Pennsylvania, 1996.

201. Lask, G., and Wagner, H.G., “Influence of Additives on the Velocity of Laminar Flames,” in *Proceedings of the Combustion Institute* **8**, 432-438, (1962).

202. MacDonald, M.A., Jayaweera, T.M., Fisher, E.M., and Gouldin, F.C., “Inhibition of Non-Premixed Flames by Dimethyl Methylphosphonate,” *Proceedings of the Central States Section*, The Combustion Institute, Pittsburgh, PA, 1997.

203. Korobeinichev, O.P., Ilyin, S.B., Mokrushin, V.V., and Shmakov, A.G., “Destruction Chemistry of Dimethyl Methylphosphonate in $H_2/O_2/Ar$ Flame Studied by Molecular Beam Mass-Spectrometry,” *Combustion Science and Technology* **116-117**, 51-67, (1996).

204. Information Handling Services, Material Safety Data Sheets Service, Microfiche Edition, Bimonthly Updates #1060-028, A-04, August/September 1989

205. Riches, J., Grant K., and Knutsen L., “Laboratory Testing of Some Phosphorus-Containing Compounds as Flame Suppressants,” 1999, in Gann, R.G., Burgess, S.R., Whisner, K.C., and Reneke, P.A., eds., *Papers from 1991-2006 Halon Options Technical Working Conferences (HOTWC)*, CD-ROM, NIST SP 984-4, National Institute of Standards and Technology, Gaithersburg, MD, (2006).

206. Riches, J., Grant K., Morey, E. and Knutsen L., “A Flame Ionization Detector As A Screening Tool For Halon Alternatives,” 2000, in Gann, R.G., Burgess, S.R., Whisner, K.C., and Reneke, P.A., eds., *Papers from 1991-2006 Halon Options Technical Working Conferences (HOTWC)*, CD-ROM, NIST SP 984-4, National Institute of Standards and Technology, Gaithersburg, MD, (2006).

207. Zegers, E.J.P., and Fisher, E.M., “Gas-Phase Pyrolysis of Diethyl Methylphosphonate,” *Combustion Science and Technology* **116-117**, 69-89, (1996).

208. Zegers, E.J.P., and Fisher, E.M., “Gas-Phase Pyrolysis of Diisopropyl Methylphosphonate,” *Combustion and Flame* **115**, 230-240, (1998).

209. Rapp, D.C., Nogueira, M.F.M., Fisher, E.M., and Gouldin, F.C., “Identification of Stable Phosphorus-Containing Combustion Byproducts by Gas Chromatography/Mass Spectrometry Preceded by Derivatization,” *Environmental Engineering Science* **14** (2), 133-140, (1997).

210. Martin, B.L., and Graves, D.J., “Hydrolysis of Trifluoroethyl Phosphate as Evidence that the Serine and Tyrosine Phosphatase Activities of Calcineurin Share the Same Specificity Determinant,” *Biochemical and Biophysical Research Communications* **194**, 150-156, (1993).

211. Roddick, D.M., and Schnabel, R.C., “(Fluoroalkyl)phosphine Coordination Chemistry,” in *Inorganic Fluorine Chemistry: Toward the 21st Century*, Thrasher, J.S., and Strauss, S.H., eds., American Chemical Society, Washington, DC, pp.421-437, 1994.

212. Johnson, D.A., *Some Thermodynamic Aspects of Inorganic Chemistry*, Ebsworth, E.A.V., Padley, P.J., and Schofield, K., eds., Cambridge University Press, London, UK, 1968, Table 7.2.

213. Sanderson, R.T., *Polar Covalence*, Academic Press, New York, NY, (1983).

214. Sanderson, R.T., *Chemical Bonds and Bond Energy*, Academic Press, New York, NY, (1976).

215. Mahler, W., “Oxidation of Tris(trifluoromethyl)phosphine,” *Inorganic Chemistry* **18** (2), 352-354, (1979).

216. Bennett, F.W., Emeléus, H.J., and Haszeldine, R.N., “Organometallic and Organometalloidal Fluorine Compounds. Part VII. Trifluoromethyl Compounds of Phosphorus,” *Journal of the Chemical Society*, 1565-1571, (1953).

217. Görg, M., Röschenthaler, G.-V., and Kolomeitsev, A.A., “Facile Syntheses of Tris(trifluoromethyl)phosphine and Difluorotris(trifluoromethyl)phosphorane,” *Journal of Fluorine Chemistry* **79**, 103-104, (1996).

218. Emeléus, H.J., and Smith, J.D., “Substitution Compounds of Tristrifluoromethylphosphine with Nickel Carbonyl,” *Journal of the Chemical Society*, 527-528,)1958).

219. Burg, A.B., Mahler, W., Bilbo, A.J., Haber, C.P., and Herring, D.L., “The Synthesis of Fluorocarbon Phosphorus Iodides,” *Journal of the American Chemical Society* **79**, 247, (1957).

220. Mahler, W., and Burg, A.B., “The Cyclopolyphosphines $(CF_3P)_4$ and $(CF_3P)_5$, and Related Chemistry,” *Journal of the American Chemical Society* **80**, 6161-6167, (1958).

221. Burg, A.B., and Street, G.B., “Perfluoromethylphosphine-Nickel Compounds, Including a New Volatile Heterocycle,” *Inorganic Chemistry* **5 (9)**, 1532-1537, (1966).

222. Emeléus, H. J., and Smith, J.D., “The Heptafluoropropyliodophosphines and Their Derivatives,” *Journal of the Chemical Society*, 375-381, (1959).

223. Phillips, I.G., Ball, R.G., and Cavell, R.G., “Synthesis and Coordination Chemistry (with Platinum(II) and Molybdenum(0)) of New Bis(bis(trifluoromethyl)phosphano)-alkanes. Structure of a New Bis(phosphano)methanide Complex,” *Inorganic Chemistry* **27**, 4038-4045, (1988).

224. Cooper, P., Fields, R., and Haszeldine, R.N., “Organophosphorus Chemistry. Part XII. Reactions of Tetramethylbiphosphine and Tetrakis(trifluoromethyl)biphosphine with Olefins,” *Journal of the Chemical Society (C)*, 3031-3035, (1971).

225. Ernst, M.F., and Roddick, D.M., “Synthesis and Coordination Properties of Bis(bis(pentafluoroethyl)phosphino)ethane,” *Inorganic Chemistry* **28**, 1624-1627, (1989).

226. Brookhart, M., Chandler, W.A., Pfister, A.C., Santini, C.C., and White, P.S., “Synthesis and Reactivity of $[(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2]Fe(CO)_3$,” *Organometallics* **11**, 1263-1274, (1992).

227. Harris, G.S., “Reactions of Halogenobistrifluoromethylphosphines with Amines and Ammonia; and their Behavior with Phosphine and Hydrogen Sulphide,” *Journal of the Chemical Society*, 512-519, 1958.

228. Burg, A.B., and Heners, J., “The New Phosphinoamines $HN[P(CF_3)_2]_2$, $CH_2N[P(CF_3)_2]_2$, and $N[P(CF_3)_2]_3$,” *Journal of the American Chemical Society* **87** (14), 3092-3097, (1965).

229. Ang, H.G., and Emeléus, H.J., “Preparation of Bistrifluoromethylamino-derivatives of Phosphorus(III) and Arsenic (III),” *Chemical Communications*, 460, (1966).

230. McElroy, M.B., Wofsy, S.C., Penner, J.E., and McConnell, J.C., “Atmospheric Ozone: Possible Impact of Stratospheric Aviation,” *Journal of the Atmospheric Sciences* **31**, 287, (1974).

231. Johnston, H.S., Kinnison, D.S., and Wuebbles, D.J., “Nitrogen Oxides from High Altitude Aircraft: An Update of Potential Effects on Ozone,” *Journal of Geophysical Research* **94**, 16351-16363, (1989).

232. Guy B., and De Rudder, A., “The Potential Impact on Atmospheric Ozone and Temperature of Increasing Trace Gas Concentrations,” *Journal of Geophysical Research* **92**, 10903-10920, (1987).

233. Miller, C., Steed, J.M., Filkin, D.L., and Jesson, J.P., “The Fluorocarbon Ozone Theory-VII. One-Dimensional Modeling-an Assessment of Anthropogenic Perturbations,” *Atmospheric Environment* **15**, 729-742, (1981).

234. Crutzen, P.J., and Arnold, F., “Nitric Acid Cloud Formation in the Cold Antarctic Stratosphere: A Major Cause for the Springtime 'Ozone Hole',” *Nature* **324**, 651-655, (1986).

235. Ioue, G., Izumi, K., and Lozovsky, V.A., “OH Reaction Rate of Halon and CFC Substitutes,” in *Development and Evaluation of Countermeasure Technologies for the Stratospheric Ozone Depletion*, Mizuno, K., and Igarashi, M., eds. Environment Agency of Japan, pp. 192-193, 1996.

236. Nelsen, O.J., Sidebotton, H.W., O'Farrell, D.J., Donlon, M., and Treacy, J., “Rate Constants for the Gas-Phase Reactions of OH Radicals and Cl Atoms with $CH_3CH_2NO_2$, $CH_3CH_2NO_2$, $CH_3CH_2CH_2CH_2NO_2$, and $CH_3CH_2CH_2CH_2CH_2NO_2$,” *Chemical Physics Letters* **156**(4), 312-318, (1989).

237. Tuazon, E.C., Carter, W.P.L.., Atkinson, R., Winer, A.M., and Pitts, J.N., Jr., “Atmospheric Reactions of N-Nitrosodimethylamine and Dimethylnitramine,” *Environmental Science and Technology* **18**, 49-54, (1984).

238. Atkinson, R., and Carter, W.P.L., “Kinetics and Mechanisms of the Gas-Phase Reactions of Ozone with Organic Compounds under Atmospheric Conditions,” *Chemical Reviews* **84**, 437-470, (1984).

239. Huheey, J.E., *Inorganic Chemistry*, 3rd Edition, Harper & Row, New York, New York, p. 301, 1983.

240. Heinonen, E.W., Lifke, J.L., and Tapscott, R.E., *Advanced Streaming Agent Development, Volume IV: Tropodegradable Halocarbons, Vol. 4 of 5*, NMERI 96/4/32540, Wright Laboratories (WL/FIVCF) and Applied Research Associates, Inc., Tyndall Air Force Base, Florida, May 1996.

241. Misaki, S., and Sekiya, A., “Development of a New Refrigerant,” presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December 1995.

242. Takahashi, K., Inomata, T., Fukaya, H., and Abe, T., “New Halon Replacements Based on Perfluoroalkylamines. An Approach from the Other Side of Fluorine Chemistry,” in *Halon Replacements Technology and Science*, ACS Symposium Series 611, Miziolek, A.W., and Tsang, W., eds., American Chemical Society, Washington, DC, Chapter 13, pp. 139-150, (1995).

243. Yasuhara, A., Kaya, K., and Shiraishi, F., “Human Impact of Halon Alternatives,” in *Development and Evaluation of Countermeasure Technologies for the Stratospheric Ozone Depletion*, Mizuno, K., and Igarashi, M., eds., Environment Agency of Japan, pp. 190-191, (1996).

244. Abe, T., Hayashi, E., Ono, T., Nishida, M., Fukaya, H., Hayakawa, Y., Terasawa, N., Inomata, T., and Takahashi, K., “Development of Halon Replacements and Their Evaluation as Fire Extinguishers,” in *Development and Evaluation of Countermeasure Technologies for the Stratospheric Ozone Depletion*, Mizuno, K., and Igarashi, M., editors, Environment Agency of Japan, pp. 187-189, (1996).

245. Haszeldine, R.N., and Tipping, A.E., “Perfluoroalkyl Derivatives of Nitrogen. Part XVII. The Reaction of N-Bromobistrifluoromethylamine with Olefins,” *Journal of the Chemical Society*, 6141-6145, (1965).

246. DesMarteu, D., O’Brien, “An Efficient Synthesis of N-Bromo perhalo-1-alkanimines,” *Journal of Organic Chemistry* **49**, 1467-1469, (1984).

247. Bauknight, C.W., and DesMarteau, D., “Reactions of N-Bromodifluoromethanimine,” *Journal of Organic Chemistry* **53**, 4443-4447, (1988).

248. O’Brien, B., Thrasher, J., Bauknight, C., Robin, M., and DesMarteau, D., N-Bromodifluoromethanimine, *Journal of the American Chemical Society* **105**, 4266-4267, (1984).

249. Visca, M., Silvani, R., and Marchionni, G., "Hydrofluoropolyethers: Another Alternative to CFCs," *Chemtech* **27** (2), 33-37, (1997).

250. Zhang, Z., Saini, R.D., Kurylo, M.J., and Huie, R.E., "Rate Constants for the Reactions of the Hydroxyl Radical with Several Partially Fluorinated Ethers," *Journal of Physical Chemistry* **96**, 9301-9304, (1992).

251. Cooper, D.L., Cunningham, T.P., Allan, N.L., and McCulloch, A., "Potential CFC Replacements: Tropospheric Lifetimes of C3 Hydrofluorocarbons and Hydrofluoroethers," *Atmospheric Environment* **27A** (1), 117-119, (1993).

252. Suga, A., Mochizuki, Y., Gotoh, Y., Ito, H., Takahashi, M., Yamashita, M., Aoyagi, M., Sekiya, A., Kondo, S., and Hakuta, T., "Estimated Lifetimes of Fluorinated Ethyl Methyl Ethers in Atmosphere," *Chemistry Express* **8 (**4), 205-208, (1993).

253. Tuazon, E.C., "Tropospheric Degradation Products of Novel Hydrofluoropolyethers," *Environmental Science and Technology* **31**, 1817-1821, (1997).

254. Imasu, R., Suga, A., and Matsuno, T., "Radiative Effects and Halocarbon Global Warming Potentials of Replacement Compounds for Chlorofluorocarbons," *Journal of the Meteorological Society of Japan* **73** (6), 1123-1136, (1995).

255. Brown, A.C., Canosa-Mas, C.E., Parr, A.D., Pierce, J.M.T., and Wayne, R.P., "Tropospheric Lifetimes of Halogenated Anaesthetics," *Nature* **341**, 635-637, (1989).

256. Misaki, S., and Sekiya, A., "Update on Fluorinated Ethers as Alternatives to CFC Refrigerants," *Proceedings, International Conference on Ozone Protection Technologies*, Washington, D.C., 21-23 October 1996, pp. 65-70.

257. Misaki, S., and Sekiya, A., "Development of a New Refrigerant," presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December 1995.

258. Sekiya, A., and Misaki, S., "Development of Hydrofluoroethers as Alternative Refrigerants and Other Applications," *Proceedings, International Conference on Ozone Protection Technologies*, Baltimore, Maryland, 12-13 November 1997, pp. 26-33.

259. *Climate Change 1995, The Science of Climate Change*, Houghton, J.T., Meira Filho, L.G., Callander, B.A., Harris, N., Kattenberg, A., and Maskell, K., eds., Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, England, 1996.

260. "Protection of Stratospheric Ozone: Notice of Acceptability," *Federal Register* **61**(173), 47012-47018, 5 September 1996.

261. Grenfell, M.W., Klink, F.W., Owens, J.G., and Yanome, H., "New Fluorinated Solvent Alternatives," presented at Precision Cleaning '95, Rosemont, Illinois, 15-17 May 1995.

262. Russell, J.P., Szur, A.J., and Terrell, R.C., "Process for making Fluorinated Ethers," U.S. patent 3,897,502, July 29, 1975, assigned to Airco, Inc., Montvale, NJ.

263. Larsen, E.R., *Fluorine Chemistry Reviews*, 1969, pp. 1-44.

264. Personal communications to J. D. Mather from Dr. J. Adcock, University of Tennessee, June/July 2005.

265. Moore, T.A., Weitz, C.A., Tapscott, R.E., "An Update on NMERI Cup Burner Test Results," 1996, in Gann, R.G., Burgess, S.R., Whisner, K.C., and Reneke, P.A., eds., *Papers from 1991-2006 Halon Options Technical Working Conferences (HOTWC)*, CD-ROM, NIST SP 984-4, National Institute of Standards and Technology, Gaithersburg, MD, (2006).

266. Darst, K.P., Ezzell, B.R., and Ishibe, N., "Preparation of a 2,3-dihaloperfluorocarbonyl halide," U.S. Patent 5,557,010), CAS# 181951-69-9, September 17, 1996, assigned to Dow Chemical Co., Midland, MI.

267. Millauer, H., Schwertfeger, W., and Siegemund, G., "Hexafluoropropene Oxide - A Key Compound in Organofluorine Chemistry," *Angewandte Chemie International Edition (English)* **24**, 161-179, (1985).

268. Carnazza, B.P., Owens, J.G., Rivers, P.E., and Schmeer, J.S., "FK-5-1-12 Performance Characteristics: Recent Developments," 2004, in Gann, R.G., Burgess, S.R., Whisner, K.C., and Reneke, P.A., eds., *Papers from 1991-2006 Halon Options Technical Working Conferences (HOTWC)*, CD-ROM, NIST SP 984-4, National Institute of Standards and Technology, Gaithersburg, MD, (2006).

269. Heinonen, E.W., Kaizerman, J.A., Lifke, J.L., Mather, J.D., Moore, T.A., and Tapscott, R.E., *Advanced Streaming Agent Development, Phase 1B: Syntheses, Toxicity, and Decomposition Products*, Final Report, NMERI 96/13/32760, Wright Laboratory, WL-TR-97-XX, 1997.

270. Personal correspondence from Carrie Weitz, NMERI, University of New Mexico, 11 November 1996, to Robert Tapscott, New Mexico Engineering Research Institute.

271. Tapscott, R. E., and Mather, J. D., "Development of a Tropodegradable Total-Flooding Agent, Phase II: Initial Screening," NMERI Report Number 96/22/30930, Advanced Agent Working Group, July 1997.

272. Yang, J.C., Manzello, S.L., Nyden, M.R., and Connaghan, M.D., "Cold Discharge of CF_3I in a Simulated Aircraft Engine Nacelle," *Proceedings of the Seventh International Symposium on Fire Safety Science,* International Association for Fire Safety Science, pp. 715-726, (2003).

273. Forbes, Lt. Col. S., "Air Force Rationale for Rejecting CF_3I as a Halon 1301 Replacement for F-16 Fuel Tank Inerting," SAF/AQRE, 12 July 2002.

274. "Suitability of CF_3I to Replace Halon 1301 as the Inerting Agent in Wing Fuel Tanks on the F-16 Aircraft," Independent Review Panel Report, HydroGeoLogic, Inc., Herndon, VA, 2002. A long summary of this report is available as Gann R. G., "Suitability of CF_3I to Replace Halon 1301 as the Inerting Agent in Wing Fuel Tanks on the F-16 Aircraft," 2003, in Gann, R.G., Burgess, S.R., Whisner, K.C., and Reneke, P.A., eds., *Papers from 1991-2006 Halon Options Technical Working Conferences (HOTWC)*, CD-ROM, NIST SP 984-4, National Institute of Standards and Technology, Gaithersburg, MD, (2006).

275. Grosshandler, W.L.; Gann, R.G.; Pitts, W.M., eds., "Evaluation of Alternative In-Flight Fire Suppressants for Full-Scale Testing in Simulated Aircraft Engine Nacelles and Dry Bays," Chapters 6, 7, and 8, NIST Special Publication 861, pp. 643-763, National Institute of Standards and Technology, Gaithersburg, MD, 1994.

276. Gann, R.G. ed., "Fire Suppression System Performance of Alternative Agents in Aircraft Engine and Dry Bay Laboratory Simulations," Volume, Chapters 5, 6, and 7, Special Publication 890, pp. 121-404, National Institute of Standards and Technology, Gaithersburg, MD, 1995.

277. Price, H.M., *Compatibility of F-16 Integral Fuel Tank Materials with* CF_3I, Report MPLR-2686, Lockheed Martin Tactical Aircraft System, October 4, 1999.

Dante, J.F., Air Force Research Laboratory Memo to Lockheed Martin, 18 Aug 2000.

278. Kenny T.J., Sheperd C.K., Hardy C.J., *Iodotrifluoromethane and Iodoheptafluoropropane Assessment of Cardiac Sensitization Potential in Dogs*, Huntingdon Research Centre. UK, for Armstrong Laboratories, Toxicology Division, Wright-Patterson AFB, OH, 1995.

279. Dodd, D.E. and Vinegar, A., "Cardiac Sensitization Testing of the Halon Replacement Candidates Trifluoroiodomethane (CF_3I) and 1,1,2,2,3,3,3-Heptafluoro-1-iodopropane (C_3F_7I)," *Drug and Chemical Toxicology* **21**(2), 137-149, (1998).

280. Hammann, S.J., Kay, M., Harper, G., Dierdorf, D., Wilson, F., "An Experimental Evaluation of CF_3I Gas Dispersion," 1997, in Gann, R.G., Burgess, S.R., Whisner, K.C., and Reneke, P.A., eds., *Papers from 1991-2006 Halon Options Technical Working Conferences (HOTWC)*, CD-ROM, NIST SP 984-4, National Institute of Standards and Technology, Gaithersburg, MD, (2006).

281. Vinegar, A., G.W. Jepson, and J.H. Overton. "PBPK Modeling of Short-term (0 to 5 min) Human Inhalation Exposures to Halogenated Hydrocarbons," *Inhalation Toxicology* **10,** 411-429 (1998).

282. Rupnik, J., Bowman, R.G., and Berrill, P., eds., *Suitability of CF_3I to Replace Halon 1301 as the Inerting Agent in Wing Fuel Tanks on the F-16 Aircraft*, Independent Review Panel Report, HydroGeoLogic, Inc., Herndon, VA, 2002. A long summary of this report is available as Gann R. G., "Suitability of CF_3I to Replace Halon 1301 as the Inerting Agent in Wing Fuel Tanks on the F-16 Aircraft," 2003, in Gann, R.G., Burgess, S.R., Whisner, K.C., and Reneke, P.A., eds., *Papers from 1991-2006 Halon Options Technical Working Conferences (HOTWC)*, CD-ROM, NIST SP 984-4, National Institute of Standards and Technology, Gaithersburg, MD, (2006).

283. Li, Y., and Wuebbles, D.J., "Potential Impacts of CF_3I as a Replacement for CF_3Br in Aircraft Applications," 2005, in Gann, R.G., Burgess, S.R., Whisner, K.C., and Reneke, P.A., eds., *Papers from 1991-2006 Halon Options Technical Working Conferences (HOTWC)*, CD-ROM, NIST SP 984-4, National Institute of Standards and Technology, Gaithersburg, MD, (2006).

284. Li, Y., Patten, G., Youn, D., and Wuebbles, D.J., "Potential Impacts of CF_3I on Ozone as a Replacement For CF_3Br in Aircraft Applications," *Atmospheric Chemistry and Physics* 6, 4559-4568, (2006).

285. DeMore, W.B., Sander, S.P., Golden, D.M., Hampson, R.F., Kurylo, M.J., Howard, C.J., Ravishankara, A.R., Kolb, C.E., and Molina, M.J., *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*, Evaluation Number 12, Jet Propulsion Laboratory (JPL) Publication 97-4, Pasadena, California, 1997.

286. Sander, S.P., Friedl, R.R., Golden, D.M., Kurylo, M.J., Huie, R.E., Orkin, V.L., Moortgat, G.K., Ravishankara, A.R., Kolb, C.E., Molina, M.J., and Finlayson-Pitts, B.J. *Chemical Kinetics and Photochemical D for Use in Atmospheric Studies*, NASA/JPL Publication 02-25, Pasadena, California, 2003.

287. Bein, D.P., "In-Flight Suppressant Deployment Temperatures," 2004, in Gann, R.G., Burgess, S.R., Whisner, K.C., and Reneke, P.A., eds., *Papers from 1991-2006 Halon Options Technical Working Conferences (HOTWC)*, CD-ROM, NIST SP 984-4, National Institute of Standards and Technology, Gaithersburg, MD, (2006).

288. Van Horn, S.R., Vitali, J., Capt. Tucker, J., Delgado, M., and Rodriguez, B., *CF_3I Agent for Fire Extinguishment in Unoccupied Areas – Aircraft Fuel Tank Inerting Application*," Technology Transition Briefing, AFRL# 99P10VA, ASC Program #292, ASC Validated Technology # 131, 1999.

289. Chattaway, A., Grigg, J., and Spring, D.J., "The Investigation of Chemically Active Candidate Halon Replacements," 1998, in Gann, R.G., Burgess, S.R., Whisner, K.C., and Reneke, P.A., eds., *Papers from 1991-2006 Halon Options Technical Working Conferences (HOTWC)*, CD-ROM, NIST SP 984-4, National Institute of Standards and Technology, Gaithersburg, MD, (2006).

290. Weast, R.C., and Grasselli, J.G., eds., *CRC Handbook of Data on Organic Compounds*, CRC Press, Inc., Boca Raton, FL, (1989).