

Alternative Fire Suppressant Chemicals: A Research Review with Recommendations

Robert E. Tapscott
Ronald S. Sheinson
Valeri Babushok
Marc R. Nyden
Richard G. Gann

NIST

National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce



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Robert E. Tapscott

GlobeTech, Inc.
Albuquerque, NM

Ronald S. Sheinson

Navy Technology Center for Safety & Survivability
Naval Research Laboratory
Washington, DC 20375

Valeri Babushok

Marc R. Nyden and Richard G. Gann

Fire Research Division
Building and Fire Research Laboratory
National Institute of Standards and Technology
Gaithersburg, MD 20899-8664

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I. INTRODUCTION

Since the signing of the Montreal Protocol on Substances that Harm the Ozone Layer in 1987 and its subsequent amendments, the use of the fire suppressant halon 1301 (CF₃Br) has declined sharply to a limited number of essential applications. Production of this chemical in the industrialized world terminated in January 1994, and the supply of halon 1301 for these essential uses is being met by established reserves. One of the essential uses is for fire protection in military and commercial aircraft.

To enable relief from dependence on this environmentally harmful substance, researchers have examined a range of chemical compounds as alternatives. The Department of Defense (DoD) Next Generation Fire Suppression Technology Program (NGP) has been a principal contributor to this search. NGP projects have examined several families of compounds, have created or adapted methods to screen these chemicals, and are developing engineering methods for making the best use of less-than-perfect alternatives to halon 1301 in military aircraft.^{1,2,3}

Supported by the DoD Strategic Environmental Research and Development Program (SERDP), the NGP is now in its fifth year, and planning is underway for the remaining years of this effort. The NGP Technical Coordinating Committee (TCC) deemed it timely to re-evaluate the world of chemistry, identify which chemical families are unlikely to contain usable alternative chemicals, which have been examined sufficiently to know that the best candidates have been already identified, and which families are still in need of scrutiny. Studies of this last group would then be included in the research plans for the remainder of the NGP. This report summarizes the efforts of a task group to perform this re-evaluation.

Such an examination requires a set of success criteria, and these have varied over time. Initially, some looked for a true drop-in replacement; where all the properties of the replacement chemical were so similar to those of halon 1301 that compatibility with the platform was complete and no subsequent modification of the fire suppression system was needed. Others looked for unique products that their companies could market. Some focused on finding high fire suppression efficiency; others looked for compounds that were free of any disqualifying property. As the field matured, several influencing factors emerged:

- For the remaining essential uses, satisfactory and affordable solutions were hard to identify. It thus became reasonable to consider chemicals with some less-than-fully-desirable behavior if the drawback(s) could be overcome.
- The list of attributes for a suppressant has evolved. For example, atmospheric lifetime has been added. Physiologically based pharmacokinetic (PBPK) modeling of the human body has shown that, for cardiac sensitization by halogenated chemicals, the toxic potency criterion need not be as limiting as had previously been thought. By contrast, there has been little resolution as to an acceptable minimal contribution to ozone depletion and global warming.
- All new weapons systems are being designed free of ozone-depleting substances, and the U.S. Army has committed to retrofitting its ground vehicles with alternate fire suppressants.

At present, the NGP is proceeding with its own set of screening criteria to define better where the search for alternative suppressants is most likely to be successful. These criteria are:

- Fire suppression and reignition quenching efficiency comparable to halon 1301 and higher than the hydrofluorocarbons (HFCs).
- Atmospheric lifetime short, on the order of a month, to keep ozone depletion, global warming, and any future adverse contributions to a minimum. This is generally a result of such tropospheric processes as photolysis, reaction with water (hydrolysis), or raining (adherence to water).

- Toxic potency of agent and combustion byproducts sufficiently low that brief exposure to an extinguishing concentration does not result in an unrecoverable injury;
- No serious interaction of the agent or its byproducts with contacted aircraft materials;
- Availability of compatible storage container components;
- Boiling point sufficiently high that a suppressing volume fraction of 5 % (at thermal equilibrium) exists at -40 °C, the minimal design temperature for aircraft suppression system performance. This boiling point is about 25 °C. Consideration was given to agents that might require a smaller concentration for suppression; for example, this boiling point criterion rises to 35 °C for a 3 % suppression concentration. Even this is not an absolute criterion, since the engine heats the interior engine nacelle surfaces during flight and since it is often feasible to warm the agent storage container. The boiling point can be as high as 75 °C if the suppression takes place in an environment at 22 °C. Of course if the agent is dispensed as a mist/powder or via a solid propellant gas generator (SPGG), the concept of a limiting boiling point criterion is not applicable.

Over the years, there has been testing and even commercializing of azeotropic blends of chemicals. Such mixtures can reduce the negative impact on people or the environment of one of the components. However, azeotropes maintain their special behavior over only a narrow range of pressure and temperature. Over the wider temperature range experienced during flight, a uniform mixture may not be maintained either within the storage container or during its discharge. In this situation, the container may not fully empty or the emerging mixture may vary in composition during the discharge period, each of these resulting in a less-than-specified residence time for an extinguishing concentration. Thus, this project did not consider the use of chemicals in blends of any type.

This document, then, reviews the state of knowledge of the fitness of chemicals as fire suppressants. In a number of cases, this has been supplemented by the judgment of the authors. Based on this compilation, the authors indicate chemical families that merit further research and, of those, the ones that are the most promising.

II. HALOGENATED ORGANIC COMPOUNDS

Compounds containing only carbon, hydrogen and oxygen, regardless of their chemical structure, are fuels rather than fire suppressants. However, when one or more halogen atoms are substituted into the structure, the compound gains the ability to quench flames. These halogenated hydrocarbons are commonly called halons. Bromine and iodine atoms are particularly effective at flame suppression, chlorine atoms less so. Remaining hydrogen atoms compromise the suppression efficiency by adding fuel to the fire.

Bromine, iodine, and chlorine atoms are also potent depleters of stratospheric ozone. However, iodine-containing compounds undergo rapid tropospheric photolysis and, therefore, have short atmospheric lifetimes, near-zero global warming potential (GWP) values, and low ozone depletion potential (ODP) values. Thus, iodine-containing compounds need no additional functionality to provide acceptable atmospheric environmental properties. On the other hand, compounds that contain no iodine, but that contain bromine and/or chlorine must possess functional groups that make the atmospheric lifetime sufficiently short to provide acceptable ODP values.

We therefore used the following principles in considering halogenated hydrocarbons as potential alternates to halon 1301:

- To obtain fire suppression performance similar to that of halon 1301, bromine or iodine (and perhaps chlorine) must be present.
- When no iodine is contained in a halocarbon, some other functionality must be present to keep the atmospheric lifetime sufficiently low to provide acceptable ODP and GWP values.
- The compounds must have some fluorine atoms to displace hydrogen in order to decrease or eliminate flammability and, in some cases, to decrease hepatotoxicity (harm to the liver).

In this section, we consider all the families of organic compounds that contain only C, H, O, and/or halogen atoms: alkanes, alkenes, alkynes, ethers, alcohols, aldehydes and ketones, aromatics. We will discuss each of these in turn, starting with members of the family that contain iodine and may contain any other halogen; then those that contain bromine and may contain fluorine and/or chlorine; then those that contain chlorine and may contain fluorine; and, finally, those that contain fluorine only. Thus, the term, for example, “bromine-containing” allows for compounds that may also contain chlorine and fluorine, but not iodine. Carboxylic acids and their esters are not considered in this report due to their expected low volatilities.

A. ALKANES

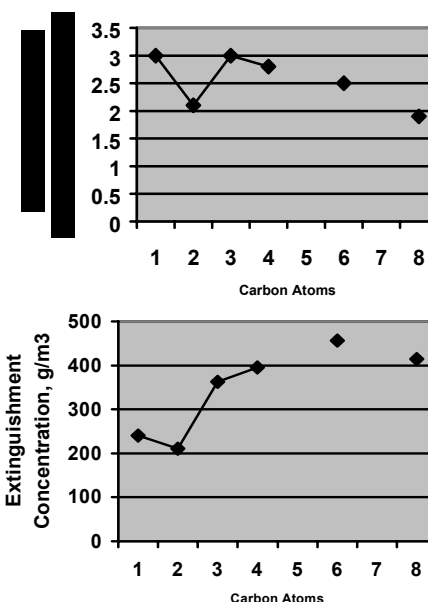
The alkanes are saturated hydrocarbons, *i.e.*, they contain only single carbon-carbon bonds.

1. Iodine-containing Alkanes

The alkyl iodides are flammable and have high boiling points. They are thus not suitable as alternatives to halon 1301. At the other extreme of iodinated alkanes are those that are fully fluorinated except for the iodine.

a. Fire Suppression Efficiency. The following table and figures show cup burner extinguishment concentrations for *n*-heptane fuel for a number of perfluorinated iodocarbons and for halon 1301 all determined with the same, non-standard, cup burner.⁴ For reference, the *n*-heptane extinguishment volume and mass fractions for halon 1301 with the cup burner specified in the NFPA Standard on Clean Extinguishing Agents⁵ are 3.4 % and 207 g/m³, respectively.⁶ Note that, generally, as the chain length increases, the extinguishment concentration expressed as volume fraction decreases, but the extinguishing concentration expressed as mass per unit volume increases. (See graphs.) The di-iodinated compound CF₂ICF₂CF₂CF₂I has a lower extinguishment concentration by volume than CF₃CF₂CF₂CF₂I, but when expressed as mass fraction, the performances of the di-iodinated and mono-iodinated compounds are almost identical. Testing with a 56 m³ (2000 ft³) compartment fire indicates that the performance of CF₃I was comparable to that of halon 1301, with any differences being due to distribution characteristics.⁷

Formula	Ext. Volume Fraction (%)	Ext. Mass Fraction (g/m ³)
CF ₃ Br	2.9	177
CF ₃ I	3.0	240
C ₂ F ₅ I	2.1	211
C ₃ F ₇ I	3.0	363
C ₄ F ₉ I	2.8	396
C ₆ F ₁₃ I	2.5	456
C ₈ F ₁₇ I	1.9	415
C ₄ F ₈ I ₂	2.1	390



b. Toxicity. The simplest and most volatile compound in this series, CF₃I, has a very low cardiac sensitization LOAEL (Lowest Observable Adverse Effect Level), a volume fraction of 0.4 %, ⁸ although the acute 4 hour rat ALC (Approximate Lethal Concentration, essentially an LC₅₀) is much higher.⁹ Toxicities of a few other fluoroiodocarbons have been determined. Noteworthy is the fact that the toxicities are highly variable. For example, perfluoropropyl iodide (CF₃CF₂CF₂I) has a 2 hour mouse LC₅₀ of 3.3 % ¹⁰ whereas 2-iodo-2-(trifluoromethyl)-1,1,1,3,3,3,4,4,4-octafluorobutane (CF₃C(CF₃)ICF₂CF₃) has a 1 hour mouse LC₅₀ of less than 0.005 %.¹¹ In spite of its relatively high LC₅₀, the former compound has a very low cardiac sensitization LOAEL of 0.1 % ¹⁰, and in this characteristic

resembles CF₃I. The only partially fluorinated fluoroiodocarbons for which toxicity data have been reported is 1,1,1-trifluoro-2-iodoethane (CF₃CH₂I), which has a 10 min mouse LC50 of 5 % and a 10 min mouse anesthetic volume fraction of 1.25 %.¹²

c. Materials Compatibility. Anhydrous iodoalkanes show good compatibility with metals although there is some possible concern about their compatibility with copper. CF₃I in particular showed no serious interaction with a number of alloys, although the interactions were an order of magnitude larger than with halon 1301.¹³ Severe corrosion can occur in the presence of water owing to hydrolysis, and this is more likely to occur with iodinated compounds than other organic halides. The compounds, of course, can react with organic polymers and elastomers may have to be carefully chosen to limit swelling and degradation. There are both elastomers and lubricants with which CF₃I is compatible.¹⁴

d. Colligative Properties. As iodination increases, boiling point (BP) increases and volatility decreases, as expected. Volatility also decreases as fluorine is replaced by hydrogen. Eventually, however, one reaches a point when most or all of the fluorine atoms have been lost that the boiling point begins to decrease. The important thing is that the boiling point is approximately 35 °C higher for iodides than for the corresponding bromides.

Formula	BP (°C)	MP (°C)	ΔH _v (kJ/mol)	Reference
CF ₃ I	-22.5	-110	22.0	5
CHF ₂ I	21.6	-122		15
CH ₂ FI	53.5			15
CH ₃ I	42.5	-66.1	27.97	15
CF ₂ I ₂	80			16
CHF ₂ I ₂	100.3	34.5		17
C ₂ F ₅ I	12			16
CF ₃ CH ₂ I	55			17
CHF ₂ CF ₂ I	39.4			16
C ₃ F ₇ I	41.2	-95.3	28 (est.) ¹⁸	19
C ₄ F ₉ I	67			16

e. Atmospheric Impact. Iodocarbons have a strong tendency to decompose photolytically, resulting in very short atmospheric lifetimes. The atmospheric lifetime of CF₃I is less than 1 day.²⁰ The atmospheric lifetime for releases at higher altitudes is thought to be significantly shorter. The estimated ODP for CF₃I is less than 0.008 and more likely 0.0001 relative to CFC-11.²⁰ If CF₃I were released directly into the stratosphere from aircraft, the ODP would be considerably higher; however, analysis indicates that high altitude releases are not a significant threat to stratospheric ozone.²¹ (Based on figures compiled by the U.S. Air Force, U.S. Navy, and commercial aircraft industry, the current release of halon 1301 during flight is less than 500 kg annually, of which about 70 kg are released at altitudes above 27 km (30,000 ft). Because this quantity is so low, expected high altitude releases of CF₃I, if used on aircraft, would not be considered a significant threat to the ozone layer.)

f. Overall Assessment. Iodides are efficient fire suppressants with low atmospheric environmental impact. The only one known to have a sufficiently low toxicity and acceptable properties to be applied to fire protection needs is CF₃I, and even this compound is unacceptable for use in normally occupied areas. There is a significant possibility that other iodides (*e.g.*, hydrofluoroiodocarbons) could have acceptable toxicities; however, the cost to determine this may be unacceptably large. While CF₃I has been well studied as a possible fire suppressant, little effort has been applied to others in this family.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied		X	
Completely unstudied			
Estimated			

2. Bromine-containing Alkanes

Here we consider all brominated alkanes whether or not fluorine and chlorine atoms are also present. Example compounds include halon 1301 (CF₃Br), HBFC-22B1 (CHF₂Br), and methyl bromide (CH₃Br). Bromoalkanes do not photolyze efficiently in the troposphere. Thus, hydrogen substitution (which makes the molecule susceptible to attack by atmospheric •OH) is needed to limit the atmospheric lifetime and the ozone depletion potential. However, if there are too many hydrogen atoms and/or carbon-carbon bonds relative to the number of halogen substituents, the compound will be an ineffective suppressant and may be flammable. This behavior is predictable.²²

a. Fire Suppression Effectiveness. The fire extinguishment effectiveness of bromine-containing alkanes is well known. Some selected *n*-heptane cup burner values are shown in the accompanying table. Note that halon 1301 extinguishment volume fractions measured using acceptable equipment and procedures range from around 2.9 % to 3.4 %. The value given here is that determined in a review of data.⁶ Hydrogenation decreases fire extinguishment effectiveness (higher extinguishment concentration); increased bromine content increases effectiveness (lower concentration). Methyl bromide is actually flammable, but can suppress a flame.

Compound	Formula	Ext. Volume Fraction (%)	Ref.
Halon 1301	CF ₃ Br	3.4	6
BFC-12B2	CF ₂ Br ₂	2.2	4
HBFC-22B1	CHF ₂ Br	3.9	23
Methyl Bromide	CH ₃ Br	5.1	24

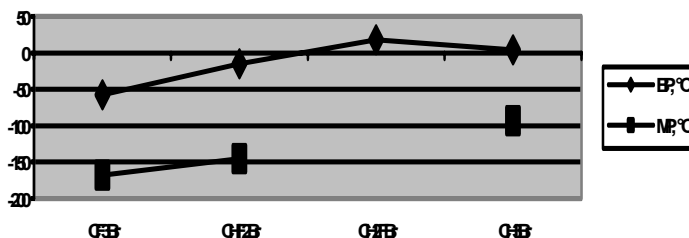
b. Toxicity. Halon 1301 appears to be the least toxic of the brominated alkanes whose toxicity has been reported. It is virtually non-toxic at design concentrations. Other brominated alkanes have varying analgesic, toxicity, and cardiotoxicity effects. The LC₅₀ values in the accompanying table (all for 4 hour exposures of rats except BFC-12B2, which is a 2 hour exposure of mice, and methyl bromide, which is an 8 hour exposure of rats) illustrate the range of toxicities encompassed by this family. In general, toxicity of bromoalkanes increases with increasing bromine content and increasing hydrogen content.

Compound	Formula	LC ₅₀ (%)	Ref.
Halon 1301	CF ₃ Br	>80	25
HBFC-22B1	CHF ₂ Br	10.8	26
Methyl Bromide	CH ₃ Br	0.03	27

c. Materials Compatibility. In general, anhydrous bromoalkanes show excellent compatibility with metals; however, severe corrosion can occur in the presence of water owing to hydrolysis. The compounds, of course, can react with organic polymers.

d. Colligative Properties. In general, as the bromination increases, the boiling point (BP), melting point (MP), and heat of vaporization (ΔH_v) increase. (See following table. The values are taken from the GlobeTech Chemical Database. References are available upon request.). In general, these properties also increase as fluorine is replaced by hydrogen. Eventually, however, one reaches a point when most or all of the fluorine atoms have been lost that these quantities start to decrease. Halon 1301 has the lowest melting point, boiling point, and heat of vaporization of any of the brominated alkanes.

Compound	Formula	MP (°C)	BP (°C)	ΔH_v (kJ/mol)
Halon 1301	CF ₃ Br	-168	-57.8	16.53
BFC-12B2	CF ₂ Br ₂	-110	24.5	25.9
HBFC-22B1	CHF ₂ Br	-145	-15.5	22.5
Methyl Bromide	CH ₃ Br	-93	3.6	24.8



e. Atmospheric Impact. With one exception, the ODP values are long for the brominated alkanes, and the materials are regulated under the Montreal Protocol. The exception is the hydrobromocarbons (HBCs). Although methyl bromide, CH₃Br, is regulated, the other HBCs are not. Moreover, some of these have relatively low toxicities and/or possibly adequate environmental properties. For example, n-propyl bromide (CH₃CH₂CH₂Br) has an ODP relative to CFC-11 of 0.006 and an atmospheric lifetime of about 11 days.²⁸ Although these compounds are flammable, they can be mixed with HFCs (or other halocarbons) to give nonflammable mixtures with good extinguishment properties.²⁹

f. Overall Assessment. ODP concerns make these compounds unacceptable for use and thus for further study.

	No Further Study	Further Study	High Priority for Further Study
Well studied	X		
Lightly studied			
Completely unstudied			
Estimated			

3. Chlorine-containing Alkanes

The fully halogenated chlorofluorocarbons have long atmospheric lifetimes and the chlorine atoms are potent ozone depleters. Elimination of use of these compounds was the principal reason for the Montreal Protocol. Thus, only the hydrochlorofluorocarbons (HCFCs), with at least one hydrogen atom to allow atmospheric •OH radical attack, can be considered.

a. Fire Suppression Effectiveness. Chlorine atoms are distinctly less efficient at effecting flame suppression than bromine or iodine atoms. As examples, HCFC-123 (CHCl_2CF_3) has a cup burner extinguishing volume fraction of approximately 7.1 %, and HCFC 22 (CHClF_2) has a value of approximately 11.6 % for *n*-heptane fuel.⁴ With this reduced chemical effect, the physical effect of an HCFC is more important; larger molecules with higher molar heat capacity require a lower mole percent for suppression. However, all HCFCs are significantly less effective than halon 1301. The nonfluorinated materials are more likely to be flammable.

b. Toxicity. Due to their applications in refrigeration, foam blowing, cleaning, and other processes to which CFCs were formerly applied, a large amount of toxicological work has been carried out on HCFCs. Overall, HCFCs have moderate to low toxic potencies. They are generally less toxic than bromofluorocarbons (CF_3Br being a major exception) and more toxic than HFCs and PFCs. Toxicity is less a drawback than environmental characteristics.

c. Materials Compatibility. Like all halocarbons, HCFCs can be corrosive toward metals in the presence of moisture. However, they are not generally corrosive when dry and are less likely to cause corrosion problems than either bromine-containing or iodine-containing compounds. Like other halocarbons, HCFCs may require careful selection of polymeric gasket materials to limit swelling and degradation.

d. Colligative Properties. HCFCs are more volatile than corresponding bromine-containing compounds. Thus, suitable compounds can be found for most or all applications based on physical properties only.

e. Atmospheric Impact. The major problem with HCFCs is that their ODP values, though low, are sufficiently large that the materials are regulated and their production will eventually be phased out. At best, they can be used only as transitional substitutes.

f. Overall Assessment. HCFCs have unacceptable environmental properties without any redeeming suppression efficiency.

	No Further Study	Further Study	High Priority for Further Study
Well studied	X		
Lightly studied			
Completely unstudied			
Estimated			

4. Fluorine-containing Alkanes

a. Fire Suppression Effectiveness. Both perfluorocarbons (PFCs) and hydrofluorocarbons (HFCs) have been widely studied as fire suppressants, and there is a very large amount of extinguishment data available at all scales. PFCs and HFCs are only moderately effective as fire extinguishants on a volume basis (see the following table of *n*-heptane cup burner values), since fluorine atoms lack the catalytic suppression chemistry of the other halogen atoms. As expected, effectiveness decreases with increasing hydrogen content, with HFC-32 being flammable.

Compound	Formula	Ext. Volume Fraction (%)	Ref.
FC-14	CF ₄	16	30
HFC-23	CHF ₃	12.3	31
HFC-32	CH ₂ F ₂	8.8	4
FC-116	C ₂ F ₆	8.1	31
HFC-125	C ₂ HF ₆	8.7	31
HFC-134a	CH ₂ FCF ₃	10	31
HFC-227ea	CF ₃ CFHCF ₃	6.3	31

b. Toxicity. As a group, the PFCs are the least toxic of all halocarbons. In fact, many of these highly stable compounds have no measurable toxicity. While the addition of hydrogen increases toxicity, HFCs still generally have low toxicity. Some HFCs have a sufficiently low cardiac sensitization that they are allowable for use in normally occupied areas. The accompanying table shows the important volume fractions for commercially available PFC and FC extinguishants and halon 1301 for comparison.^{25,32}

Compound	LC ₅₀ (%)	NOAEL (%)	LOAEL (%)
Halon 1301		5	7.5
HFC-23	>65	50	>50
HFC-125	>70	7.5	10.0
HFC-227ea	>80	9.0	10.5
HFC-236fa	>18.9	10	15
FC-218	>81	30	>30
FC-3-1-10	>80	40	>40

c. Materials Compatibility. PFCs and HFCs are probably the least corrosive of any halocarbons. Problems can still exist with wet materials, but the high strength of the C-F bond makes hydrolysis difficult. PFCs are not compatible with some fluorinated polymers; but compatible elastomers exist.

d. Colligative Properties. HFCs and PFCs have physical properties ideal for halon replacement. These compounds are more volatile than their bromine-containing counterparts.

e. Atmospheric Impact. HFCs and PFCs have no significant ozone depletion, however, HFCs and, in particular, PFCs have long atmospheric lifetimes and high global warming. The following table shows the environmental properties of the HFC and PFC fire extinguishants now being commercialized with halon 1301 for comparison.³³

Agent	ODP	GWP	Atmospheric Lifetime (yrs)
Halon 1301	12-16	5600	65
HFC-23	0	1210	250
HFC-125	0	3200	36
HFC-227ea	0	3300	41
HFC-236fa	0	8000	250
FC-218	0	6100	3200
FC-3-1-10	0	5500	2600

f. Overall Assessment. These compounds have been well studied and are becoming widely marketed for a wide range of applications. However, for aircraft use, the relatively poor environmental properties and the mediocre extinguishment efficiencies suggest no further study is needed.

	No Further Study	Further Study	High Priority for Further Study
Well studied	X		
Lightly studied			
Completely unstudied			
Estimated			

A. ALKENES

1. Iodine-containing Alkenes

Iodoalkenes are a family that contains two functionalities, both of which are likely to contribute to lower stability relative to the alkanes. The carbon-iodine bond is rather weak and the carbon-carbon double bond is reactive. Iodine-containing compounds are also subject to hydrolysis.

a. Fire Suppression Effectiveness. To the best of our knowledge, no extinguishment studies have been carried out on any iodoalkene. The effect of the double bond on extinguishment is uncertain; however, it is known that some highly halogenated, lower molecular weight alkenes are flammable.³⁶

b. Toxicity. There are no published data. Due to their expected low stability and the possibility of alkylation, iodoalkenes are likely to be more toxic than many of the other halocarbons being considered.

c. Materials Compatibility. Because of their reduced stability and the potential formation of HI upon hydrolysis, it is expected that materials compatibility will be of concern with iodine-containing alkenes.

d. Colligative Properties. Volatility is likely to be lower than the bromoalkenes. The boiling point of the simplest iodoalkene, vinyl iodide, is 56 °C, 40 °C higher than the comparable bromide. Fluorination could reduce these values.

e. Atmospheric Impact. With expected rapid photolysis and the susceptibility of the double bond to attack by atmospheric •OH, iodine-containing alkenes are expected to have exceedingly short atmospheric lifetimes and near-zero GWP and ODP values.

f. Overall Assessment. These compounds have been completely unstudied as fire suppressants. A screening study is recommended even though the compounds have possible stability and toxicity problems.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied		X	
Completely unstudied			
Estimated			

2. Bromine-containing Alkenes

a. Fire Suppression Effectiveness. A number of flame extinguishment studies have been carried out on bromofluoroalkenes and hydrobromofluoroalkenes. The cup burner values for *n*-heptane fuel in the following table have been taken from several sources.^{34,35,4,31} Most of these compounds have extinguishment concentrations at least as low as halon 1301 on a volume basis. The substituted ethylenes appear to be significantly poorer extinguishing agents than the higher molecular weight materials. The effect of the double bond on extinguishment is uncertain; however, it is known that some highly halogenated, lower molecular weight alkenes, e.g., $\text{CF}_2=\text{CFBr}$, are flammable.³⁶ Recent unreported work indicates that in larger scale testing, $\text{CH}_2=\text{CBrCF}_3$ greatly outperforms HFC-227ea.³⁷ Testing using the Dispersed Liquid Agent Fire Suppression Screen (DLAFSS) apparatus developed by the National Institute of Standards and Technology indicates a fire suppression capability for $\text{CH}_2=\text{CBrCF}_3$ comparable to or possibly better than that of halon 1301³⁴, although precise comparison between the two agents is difficult with the DLAFSS apparatus because of differences in their dispersion.

Bromoalkene	Ext. Volume Fraction (%)
$\text{CHBr}=\text{CHCF}_3$	3.5
$\text{CH}_2=\text{CHCBrF}_2$	4.5
$\text{CH}_2=\text{CBrCF}_3$	2.6
$\text{CH}_2=\text{CHCF}_2\text{CBrF}_2$	3.5
$\text{CH}_2=\text{CHCClFCBrF}_2$	4.5
$\text{CH}_2=\text{CBrCF}_2\text{CF}_3$	3.8
$\text{CBrF}=\text{CF}_2$	6.3
$\text{CHBr}=\text{CF}_2$	6.0
$\text{CH}_2=\text{CBrCF}_2\text{CF}_2\text{CF}_3$	3.7
$\text{CH}_2=\text{CBrCF}(\text{CF}_3)\text{CF}_3$	3.3
$\text{CH}_2=\text{CBr}(\text{OCF}_3)\text{CF}_3$	3.8
$(\text{CF}_3)_2\text{C}=\text{CHBr}$	2.6
$\text{CF}_3\text{CF}_2\text{CH}=\text{CHBr}$	3.1

b. Toxicity. Acute inhalation toxicity testing has been performed on a limited number of hydrobromofluoroalkenes, as shown in the following table.³⁵ The test exposure protocol used a 30 min exposure of 10 rats (5 male and 5 female) to each chemical at a volume fraction of 5 % in air. Following the exposure the animals were removed from the exposure apparatus, observed for 2 hours, and then sacrificed for examination of tissues. The compounds had much lower toxicity than expected. Other recent studies have shown negative results for chromosomal aberration tests³⁸ and Ames tests³⁵ on some hydrobromofluoroalkenes.

Bromoalkene	Deaths	Necropsy Result
$\text{CH}_2=\text{CBrCF}_3$	0	All tissues normal
$\text{CHBr}=\text{CHCF}_3$	0	All tissues normal
$\text{CH}_2=\text{CHCBrF}_2$	7	Lungs mottled
$\text{CH}_2=\text{CHCF}_2\text{CBrF}_2$	0	All tissues normal
$\text{CH}_2=\text{CBrCF}_2\text{CF}_3$	0	Lungs mottled
$\text{CH}_2=\text{CBrCF}_2\text{CF}_2\text{CF}_3$	1	Lungs mottled
$\text{CH}_2=\text{CBrCF}(\text{CF}_3)_2$	10	Lungs marked mottling

c. Materials Compatibility. Bromine-containing alkenes will generally be more reactive than the corresponding alkanes. Nevertheless, there is no reason to expect compatibility problems that cannot be overcome with suitable materials. As with all halocarbons, metal corrosion will be increased by the presence of water, which causes hydrolysis.

d. Colligative Properties. The requirement for at least two carbon atoms (to allow formation of a carbon-carbon double bond), the probable need to use propene and higher molecular weight derivatives to obtain good fire suppression, and the requirement for at least one bromine atom, gives these compounds a higher molecular weight and therefore a lower volatility than some other halocarbon families. To date, the lowest boiling point material for which fire extinguishment testing has been performed has been 2-bromo-3,3,3-trifluoropropene, $\text{CF}_3\text{CBr}=\text{CH}_2$, which has a boiling point of 34 °C. The fully halogenated propene $\text{CF}_2=\text{CFCBrF}_2$ has a boiling point of 28 °C³⁹, and this may represent a lower limit for the compounds with three or more carbon atoms. Only a few heat of vaporization values have been reported or estimated for bromofluoroalkenes and hydrobromofluoroalkenes. These tend to be around 30 kJ/mol.

e. Atmospheric Impact. Atmospheric lifetimes, GWP values, and ODP values are believed to be very low for bromine-containing alkenes. Recent, yet unpublished work confirms this.⁴⁰ Estimated lifetimes for three bromofluoroalkenes based on measured reactivity towards $\bullet\text{OH}$ are 3.2 days for $\text{CH}_2=\text{CBrCF}_3$, 3.4 days for $\text{CH}_2=\text{CBrCF}_2\text{CF}_3$, and 7.3 days for $\text{CH}_2=\text{CHCF}_2\text{CF}_2\text{CBrF}_2$. These values imply very low ODP and GWP values.

f. Overall Assessment. Although the lower volatility will adversely affect the usage envelope, bromine-containing alkenes are probably the most promising halon replacements discovered to date. A fuller look at this family is thus warranted. There may be a higher probability of success for streaming agent substitutes.

	No Further Study	Further Study	High Priority for Further Study
Well studied			X
Lightly studied			
Completely unstudied			
Estimated			

3. Chlorine-containing Alkenes

a. Fire Suppression Effectiveness. No data are available on the extinguishing performance of chlorine-containing alkenes. It is expected that the higher energy content of the double bond will decrease performance relative to the corresponding alkane. A chlorine atom adds less effectiveness compared to that provided by bromine or iodine.

b. Toxicity. No toxicity studies on chlorofluoroalkenes and hydrochlorofluoroalkenes have been reported. It is known that a number of nonfluorinated chlorine-containing alkenes are rather toxic.

c. Materials Compatibility. Chlorine-containing alkenes will be, as a whole, less reactive than the corresponding bromine compounds, but higher in reactivity than the chlorine-containing alkanes. Nevertheless, there is no reason to expect compatibility problems that cannot be overcome with suitable materials. As with all halocarbons, metal corrosion will be increased by the presence of water, which causes hydrolysis.

d. Colligative Properties. Little information is available on chlorofluoroalkenes and hydrochlorofluoroalkenes. The physical properties of these compounds are likely to be more suitable for total flood fire protection than the bromine-containing alkenes.

e. Atmospheric Impact. Due to the presence of a double bond, chlorine-containing alkenes are expected to have very low atmospheric lifetimes, global warming potentials, and ozone depletion potentials.

f. Overall Assessment. The chlorine-containing alkenes are not expected to have sufficient fire extinguishment capability to justify the studies required to better characterize these compounds as extinguishants. Toxicity also remains a major concern.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied			
Completely unstudied			
Estimated	X		

4. Fluorine-containing Alkenes

a. Fire Suppression Effectiveness. Only two compounds in this category have been investigated for flame suppression. Hexafluoropropene ($\text{CF}_2=\text{CFCF}_3$) has a heptane cup burner extinguishment volume fraction of 7.3 %³¹, and octafluoro-2-butene ($\text{CF}_3\text{CF}=\text{CFCF}_3$) is reported to have a cup burner extinguishment volume fraction of 4.9 %.⁴¹ The latter value may be low since this determination is believed to have been made using an apparatus known to give low values in other cases. The analogous fully fluorinated saturated compounds are perhaps slightly more efficient, 6.1 %⁴² and 5.3 %, respectively.³¹

b. Toxicity. The toxicity of the few perfluoroalkenes and hydrofluoroalkenes whose toxicity has been studied is surprisingly high. $\text{CF}_3\text{C}(\text{CF}_3)=\text{CFCF}_2\text{CF}_3$ has a 1 hour mouse LC_{50} of 0.0175 %¹¹; and in an anesthesia test, all mice exposed to a volume fraction of 0.8 % to 3.4 % of 1-methylnonafluorocyclohexene died, as did all those exposed to 0.8 % to 1.5 % of decafluorocyclohexene and to 3.0 % to 7.3 % (6 min) of octafluorocyclopentene⁴³. On the other hand, the 10 min LC_{50} for $\text{CH}_2=\text{CHCF}_2\text{CH}_3$ is a moderately high 25 %, and the 4 hour LC_{50} for $\text{CF}_2=\text{CFCF}_3$ is 1.12 %.⁴⁴ The very high molecular weight compound $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}=\text{CHCF}_2\text{CF}_2\text{CF}_2\text{CF}_3$ has been used as a blood substitute.¹⁸

c. Materials Compatibility. Although more reactive than the PFCs and HFCs, hydrofluoroalkenes and perfluoroalkenes are expected to have relatively good corrosion and compatibility properties. Again it is expected that fluoropolymers may be incompatible with these materials, but other elastomers are undoubtedly available.

d. Colligative Properties. The accompanying table shows some of the important colligative properties of selected perfluoroalkenes and hydrofluoroalkenes. The ΔH_v values are at the normal boiling points. In general, unsaturation leads to a very slight increase in boiling point when compounds are compared to saturated compounds with the same number of carbon atoms. The physical properties of the materials are suitable for total flood applications.

Formula	MP (°C)	BP (°C)	ΔH_v (kJ/mol)
$\text{CH}_2=\text{CHCF}_2\text{CH}_3$		24 ¹²	
$\text{CF}_2=\text{CFCF}_3$	-156 ¹⁸	-29 ¹⁸	21 ⁴⁵
$\text{CH}_2=\text{CHCF}_3$		-24 ¹²	24 ¹⁸ (est.)
$\text{CF}_2=\text{CHCF}_3$		-17 to -16 ³⁹	23 ¹⁸ (est.)
$\text{CF}_3\text{CH}=\text{CHCH}_3$		17.7 ³⁹	
$\text{CF}_3\text{CF}=\text{CFCF}_3$		0 ¹⁸	21 ¹⁸ (est.)
$\text{CF}_3\text{CH}=\text{CHCF}_3$		6 ¹⁸	26 ¹⁸ (est.)
$(\text{CF}_3)_2\text{C}=\text{C}(\text{CF}_3)_2$		55 ¹⁸	29 ¹⁸
$\text{CF}_2=\text{CF}_2$	-142.5 ¹⁵	-75.9 ¹⁵	

e. Atmospheric Impact. Unsaturation significantly reduces the atmospheric lifetime. For example, perfluoropropane has a lifetime of 2600 years⁴⁶, while hexafluoropropene has a lifetime of only 5.8 days.⁴⁷ Global warming and atmospheric persistence will not be problems with the fluorinated alkenes, and these materials have no ozone depletion potential.

f. Overall Assessment. Perfluorinated alkenes and hydrofluoroalkenes have excellent atmospheric environmental properties, but they are expected to be no better than the perfluorocarbons and HFCs in fire protection and may be worse. The only reason to consider these materials is if environmentally superior HFC-like materials are required.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied	X		
Completely unstudied			
Estimated			

B. Alkynes

Alkynes contain carbon-carbon triple bonds. The bonds to adjacent atoms or groups are weakened and thus substituted alkynes should undergo reaction in the troposphere. The bond weakness may also lead to stability and manufacturing difficulties

a. Fire Suppression Effectiveness. Nothing is known of the fire suppression characteristics of haloalkynes. Bromine and iodine would impart some fire suppression capability, but the higher energy content of the triple bond will offset this. Compounds containing iodine or bromine directly attached to a triply bonded carbon are known to be unstable. Diiodoacetylene is explosive; some bromoalkynes are pyrophoric. The halogen could, of course, be attached to an alkyl substituent.

b. Toxicity. Nothing is known of the toxicity of the haloalkynes. In view of the expected low stability, however, toxicity is likely to be high.

c. Materials Compatibility. It is likely that haloalkynes will have poorer material compatibility properties than most other halocarbons discussed in this report; however, nothing concrete is known.

d. Colligative Properties. Insufficient data are available on lower molecular weight haloalkynes to make any determination of physical property trends. More information is available on very large iodine-containing alkynes, which are used in organic syntheses.

e. Atmospheric Impact. Tropospheric reactions with tropospheric $\bullet\text{OH}$ (and photolysis) are likely to limit atmospheric lifetimes and make contributions to ozone depletion and global warming negligible.

f. Overall Assessment. Other than the expected good atmospheric environmental properties, there is no obvious advantage to haloalkynes. Their stability is likely to be low and there may also be manufacturing difficulties.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied			
Completely unstudied	X		
Estimated			

C. Ethers

These compounds contain a C-O-C grouping, which contributes to reactivity in the troposphere.

1. Iodine-Containing Ethers

- a. Fire Suppression Effectiveness.** Nothing is known about the effectiveness of the iodinated derivatives. There is no reason to believe that the suppression capabilities will significantly differ from those of the fluoroiodoalkanes, the hydrofluoroiodoalkanes, or the equivalent brominated compounds.
- b. Toxicity.** Hydrofluoroethers and perfluoroethers can have low toxicity. The effect of iodine substitution is unknown, but it is expected that the toxicity will increase due to the low C-I bond strength.
- c. Materials Compatibility.** The materials compatibility of iodine-containing ethers is unknown. It is possible that such compounds may exhibit slightly worse compatibility than the corresponding alkanes due to the small polarity induced by the oxygen atom.
- d. Colligative Properties.** Little information is available. The lightest iodine-containing ether, iodomethyl methyl ether (iodomethoxymethane) has a relatively high boiling point of 122 °C at 1 atm.⁴⁸ 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, compounds will have properties that are less than suitable for total flood application.
- e. Atmospheric Impact.** The presence of iodine should lead to short atmospheric lifetimes, as with the other iodinated compounds. This would lead to very low ODP and GWP values. The ether linkage is likely a secondary contributor.
- f. Overall Assessment.** If the iodine-substituted alkanes do not produce an acceptable candidate, this family might be worth screening. However, the high boiling point is a deterrent for total flooding applications. The only reason to use iodine-substituted ethers is to provide a way to modify the properties to improve toxicity, performance, stability, materials compatibility, or other characteristics.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied			
Completely unstudied	At present		
Estimated			

2. Bromine-containing Ethers

a. Fire Suppression Effectiveness. Some bromination of these compounds is needed to decrease flammability. Only two studies of fire suppression by of hydrobromofluoroethers (HBFEs) have been carried out. $\text{CH}_2=\text{CBr}(\text{OCF}_3)\text{CFCF}_3$, which is unsaturated, has a cup burner extinguishment concentration of 3.8 volume percent.³⁵ $\text{CH}_3\text{-O-CF}_2\text{CHBrF}$ has been estimated to have a heptane cup burner volume fraction of 4.2 %.³⁶ These extinguishing concentrations seem high, given the presence of a bromine atom plus the physical cooling from the compounds' relatively high molecular weights. The hydrobromochlorofluoroether $\text{CBrF}_2\text{-O-CF}_2\text{CHClF}$, has been suggested as an example of a chemical to be tested for fire suppression efficiency.¹⁸

b. Toxicity. Some very limited toxicity results are available for HBFEs; however, much more work is needed to estimate the tolerability of the toxicity of this family. $\text{CH}_3\text{-O-CF}_2\text{CHBrF}$ has been reported to be a good anesthetic at a volume fraction of 2.5 %.⁴⁹ $\text{CBrF}_2\text{CF}_2\text{-O-CH}_3$ has been estimated to have a 2 hour mouse LC_{50} of 0.84 % based on a quantitative structure-activity relationships (QSAR).⁵⁰ A minimum anesthetic volume fraction of 0.8 % and a minimum lethal volume fraction of 1.5 % have been reported for $\text{CHFBrCF}_2\text{CH}_2\text{-O-CH}_3$.⁵¹ $\text{CHF}_2\text{-O-CF}_2\text{CHBrF}$ has been reported to be a good anesthetic in mice at a volume fraction of 1.9 %⁵² and $\text{CH}_3\text{-O-CF}(\text{CF}_3)\text{CBrF}_2$ has been reported to produce anesthesia in mice with excitation at a volume fraction of 5 %.⁴⁹

c. Materials Compatibility. No information is available on material compatibility for the HBFEs; however, compatibilities better than the hydrobromofluoroalkenes and slightly worse than the HBFCs are expected.

d. Colligative Properties. Boiling points for the HBFEs in the GlobeTech Database (references available on request) and for HFEs obtained from some HBFEs by substitution of fluorine for bromine are shown in the following table. Few data are available for low molecular weight HBFEs.

Formula	HBFE BP (°C)	HFE BP (°C)
$\text{CH}_3\text{-O-CF}=\text{CBrF}$	67	
$\text{CH}_3\text{-O-CF}=\text{CBrF}$	59	
$\text{CH}_3\text{CH}_2\text{-O-CF}_2\text{CH}_2\text{Br}$	70	
$\text{CF}_3\text{-O-CH}_2\text{CH}_2\text{Br}$	78.5	
$\text{CH}_3\text{-O-CF}_2\text{CHBrF}$	88.8	37.2
$\text{CHFBrCF}_2\text{CH}_2\text{-O-CH}_3$	125	66
$\text{CH}_3\text{CH}_2\text{-O-CF}_2\text{CHFBr}$	106	57
$\text{CH}_2\text{BrCH}=\text{CFCF}_2\text{-O-CH}_3$	74	
$\text{CH}_3\text{CH}_2\text{CH}_2\text{-O-CF}_2\text{CHFBr}$	75.2	
$\text{CHF}_2\text{-O-CF}_2\text{CHBrF}$	73	28.5
$\text{CH}_3\text{-O-CF}(\text{CF}_3)\text{CBrF}_2$	80	
$\text{CH}_3\text{CH}_2\text{-O-CF}_2\text{CHBr}_2$	65	
$\text{CBrF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{-O-CH}_2\text{CH}_3$	185.7	
$\text{CH}_3\text{CH}_2\text{CH}_2\text{-O-CF}_2\text{CHBr}_2$	72.2	
$\text{CH}_2=\text{CBr}(\text{OCF}_3)\text{CFCF}_3$	75	
$\text{CF}_3\text{CHBrCH}_2\text{-O-CH}_2\text{CHBrCF}_3$	167	
$\text{CF}_3\text{CHBrCH}_2\text{-O-CH}_2\text{-O-CH}_2\text{CHBrCF}_3$	195	
$\text{CH}_3\text{-O-CF}_2\text{CHBr}_2$	55.8	
$\text{CF}_3\text{CBrFCH}_2\text{-O-CH}_2\text{-O-CH}_2\text{CBrFCF}_3$	92	
$\text{CH}_3\text{-O-CF}_2\text{CH}_2\text{Br}$	54.7	

The boiling point for $\text{CBrF}_2\text{-O-CF}_3$ (not an HBFE) has been estimated as $-30\text{ }^\circ\text{C}$.¹⁸ This appears to be low. For four compounds (see table column marked HFE) substitution of Br for F causes an average boiling point increase of $52\text{ }^\circ\text{C}$. Since $\text{CF}_3\text{-O-CF}_3$ has a boiling point of $-59\text{ }^\circ\text{C}$, $\text{CBrF}_2\text{-O-CF}_3$ is expected to have a boiling point of $-8\text{ }^\circ\text{C}$. Similarly, $\text{CH}_3\text{-O-CF}_3$ has a boiling point of $-24.2\text{ }^\circ\text{C}$, and $\text{CH}_3\text{-O-CBrF}_2$ is predicted to have a boiling point of $28\text{ }^\circ\text{C}$. 3-carbon compounds (*e.g.*, $\text{CH}_3\text{-O-CF}_2\text{CHBr}_2$, BP = $55.8\text{ }^\circ\text{C}$) will have marginally acceptable boiling points for use as total flooding agents. The HBCFE $\text{CBrF}_2\text{-O-CF}_2\text{CHClF}$ has been estimated to have $\Delta H_v = 30.3\text{ kJ/mol}$ (115 kJ/kg) at the normal boiling point and a vapor phase heat capacity of 175 J/mol-K (664 J/kg-K) at $25\text{ }^\circ\text{C}$.⁴⁹

e. Atmospheric Impact. These compounds should have low environmental impact.³⁴ Some hydrogen content is needed to provide sites for attack by atmospheric $\bullet\text{OH}$ since the C-O-C linkage is insufficiently polar to provide fast rainout. Only limited studies have been made of the kinetics of reactions of bromoethers with $\bullet\text{OH}$.⁵³ The lifetime of $\text{CH}_3\text{-O-CF}_2\text{CHBrF}$ has been estimated as 14 and 50 days.³⁶ At this time, too few data exist to estimate ODP values, but the preceding lifetime estimates suggest the values would be low.

f. Overall Assessment. These compounds may be sufficient, although not outstanding extinguishants. Before going further, it is essential that we have good information on atmospheric environmental properties. Below, we state that the compounds have been lightly studied; in fact, however, they are almost unstudied.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied		X	
Completely unstudied			
Estimated			

3. Chlorine-containing Ethers

a. Fire Suppression Effectiveness. No fire suppression testing has been carried out for a chlorine-containing ether; however, the compounds 2-chloro-1,1,2-trifluoro-1-(difluoromethoxy)ethane ($\text{CHF}_2\text{-O-CF}_2\text{CHClF}$) and 2-chloro-1,1,1-trifluoro-2-(difluoromethoxy)ethane ($\text{CHF}_2\text{-O-CHClCF}_3$) have been suggested as representative of chlorine-containing ethers for fire suppression testing.¹⁸ HCFEs are likely to have fire suppression efficiencies greater than those of the hydrofluoroethers, but well below the efficiencies of bromine-containing compounds.

b. Toxicity. In general, fluorination is probably needed to keep the hepatic toxicity reasonable. Some chlorine-containing ethers have been considered as anesthetics and therefore have reasonable acute toxicities (although they may have anesthesia problems). Examples are 2-chloro-1-methoxy-1,1,2-trifluoroethane (halomar), 2,2-dichloro-1,1-difluoro-1-methoxyethane ($\text{CH}_3\text{-O-CF}_2\text{CHCl}_2$, methoxyflurane), $\text{CHF}_2\text{-O-CF}_2\text{CHClF}$ (enflurane), and $\text{CHF}_2\text{-O-CHClCF}_3$ (forane). Methoxyflurane is reported to be anesthetic in mice at a volume fraction of 1.25 %⁵⁴, and enflurane is reported to be a good anesthetic in mice at a volume fraction of 1.9 %.⁵² It is expected that the presence of chlorine will make the toxicities a little worse than those of the corresponding hydrofluoroethers, some of which have reasonable toxicities.

c. Materials Compatibility. No information is available for the materials compatibility with HCFEs. These compounds are, however, expected to have no serious compatibility problems. They are likely to have compatibilities similar to, but a little more problematical, than those of the hydrofluoroethers.

d. Colligative Properties. Data are available for a few chlorine-containing ethers, particularly since some have been considered as anesthetics. For methoxyflurane (with two Cl atoms), BP = 105 °C⁵⁴; for enflurane, BP = 56.5 °C⁵²; and for forane, BP = 48.5 °C.⁵⁵ Estimates of $\Delta H_v = 29.4$ kJ/mol (159 kJ/kg) at the normal boiling point and vapor phase heat capacity = 162 J/mol-K at 25°C have been made for enflurane and, under the same conditions) of $\Delta H_v = 28.7$ kJ/mol (156 kJ/kg) and vapor phase heat capacity = 167 J/mol-K for forane.¹⁸ The unsaturated 1-chloro-1,2-bis(trifluoromethoxy)ethene ($\text{CF}_3\text{-O-CH=CCl-O-CF}_3$) has a boiling point of 54 °C.⁵⁶ Three-carbon derivatives (*e.g.*, forane) should have boiling points that are at the edge of acceptability as total flooding agents. The vapor pressures of four-carbon HCFEs are likely to be too low.

e. Atmospheric Impact. In a number of cases, the presence of an ether linkage significantly increases reaction rates with tropospheric •OH; however, this is not true in all cases.⁵⁷ It is likely that substitution of chlorine for fluorine will cause a decrease (though probably small) in atmospheric lifetime. Since some hydrofluoroethers are known to have atmospheric lifetimes, in the best of cases, of under a year, the HCFEs are likely to be, at best, marginally acceptable.

f. Overall Assessment. Since the HCFEs will operate mainly by heat absorption and are likely to be only marginally better than the hydrofluoroethers in fire suppression, and since these compounds are likely to have at best marginally acceptable environmental characteristics, it is recommended that no studies be performed.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied			
Completely unstudied	X		
Estimated			

4. Fluorine-containing Ethers

a. Fire Suppression Effectiveness. These are primarily physical agents. Fluorine is needed primarily to keep the flammability low and secondarily to control the physical properties. Cup burner flame suppression capabilities for three HFEs with *n*-heptane fuel are shown in the following table.⁴¹ In addition, flame suppression values for butane fuel using a micro cup burner have been reported for C₄F₉-O-C₂H₅ (6.5 volume percent, 701 g/m³) and CH₃-O-C₃F₇ (7.5 volume percent, 613 g/m³).⁵⁸ A mixture of hydrofluoropolyethers has been shown to have an *n*-heptane cup burner value of 5.1 volume percent.⁵⁹ Some larger scale testing of methyl perfluoro-*n*-butyl ether has been carried out. This agent can exceed halon 1301 efficiency if delivered as a mist, thus realizing the endothermicity of vaporization.

Formula	Ext. Vol. Fraction (%)	Ext. Conc. (g/m ³)
CHF ₂ -O-CF ₃	8.6	480
CHF ₂ -O-CH ₂ CF ₃	11.7	720
CH ₃ -O-C ₄ F ₉ (HFE-7100)	6.1	620

b. Toxicity. Ethers have relatively low toxicities due to the low reactivity of the C-O-C functional group arising from the strength of the C-O bond. Several volatile ethers can affect the central nervous system. A substantial amount of data is available for HFCs since a number have been considered as alternative refrigerants and solvents. Most of the HFEs examined exhibit relatively low toxicities and are not mutagenic. A survey of toxicities for HFEs is available.⁶⁰

c. Materials Compatibility. HFEs are expected to have compatibility properties at least as good as those of halon 1301. Some limited results may be available from research being performed (primarily in Japan) on HFE refrigerants.

d. Colligative Properties. A large amount of physical property data is available for the HFEs. The two-carbon compounds will, of course, have the lowest boiling points. The boiling point of CHF₂-O-CF₃ is -35 °C⁶¹ and that of CHF₂-O-CHF₂ is 5 °C.⁶² The fully fluorinated material, CF₃-O-CF₃, has a boiling point of -59 °C.

e. Atmospheric Impact. Ethers that contain no iodine, bromine, or chlorine have no ODP; however, atmospheric lifetimes may still be a problem. In fact, perfluoroethers are expected to have atmospheric lifetimes similar to those of the perfluorocarbons and thus to be partially fluorinated to be acceptable. Lifetimes and GWP values as low as 0.3 years and 39 (100 year time horizon, relative to CO₂) have been found for HFEs.⁵⁷ However, some HFEs have considerably longer lifetimes and higher GWP values.

f. Overall Assessment. There has been extensive examination of this family, and HFE-7100 has emerged as the optimal candidate.

	No Further Study	Further Study	High Priority for Further Study
Well studied	X		
Lightly studied			
Completely unstudied			
Estimated			

D. Alcohols

Alcohols contain one or more hydroxyl (-OH) groups attached to carbon atoms.

1. Iodine-containing Alcohols.

In this section, we consider alcohols that contain iodine and may contain other halogens.

a. Fire Suppression Effectiveness. No extinguishment data have been reported for iodine-containing alcohols. Like other iodine-containing materials, these are expected to have good extinguishment properties.

b. Toxicity. The toxicities of iodine-containing alcohols are unknown. It is expected that they will be more toxic than the iodine-containing alkanes, which in some cases to have very low cardiac sensitization levels.^{8,10}

c. Materials Compatibility. Iodine-containing alcohols are expected to be more reactive toward metals than iodine-containing alkanes. There may be self reactions (*e.g.*, $\text{CH}_2\text{IOH} \rightarrow \text{O}=\text{CH}_2 + \text{HI}$ or $2\text{CH}_2\text{ICH}_2\text{OH} \rightarrow \text{CH}_2\text{ICH}_2\text{-O-CH}_2\text{CH}_2\text{OH} + \text{HI}$) forming highly corrosive hydrogen iodide.

d. Colligative Properties. A few iodine-containing alcohols have been reported and some of these are commercially available. Unfortunately, many of those commercially available have very large molecular weights (3-Perfluorohexyl-2-iodopropan-1-ol, MP = 49 °C, BP = 90 °C at 0.2 kPa; 3-(perfluoro-5-methylhexyl)-2-iodopropanol, BP = 88 °C to 90 °C at 0.2 kPa.⁶³ 2-Iodoethanol has a relatively high boiling point of 85 °C at 3.3 kPa.

e. Atmospheric Impact. Iodine-containing alcohols are expected to have exceedingly short atmospheric lifetimes. They should both rain out and photolyze rapidly. The GWP values and ODP values are expected to be near zero.

f. Overall Assessment. An alcohol functionality is not needed when iodine is present in the molecule, and is expected to increase toxicity. There is no obvious advantage for consideration of iodine-containing alcohols.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied			
Completely unstudied	X		
Estimated			

2. Bromine-containing Alcohols

In this section, we consider alcohols that contain bromine and may also contain chlorine and/or fluorine.

a. Fire Suppression Effectiveness. Little information is available; however, these compounds should be as effective as other brominated compounds. $\text{CF}_3\text{CHOHCH}_2\text{Br}$ has been reported to have an *n*-heptane cup burner extinguishment volume fraction of 4.1 %, 323 g/m³.⁶⁴ This compound has been reported to extinguish an H_2/CH_4 flame in an FID at a volume fraction of 3 %.⁶⁵ An *n*-heptane cup burner extinguishment volume fraction of 4.87 %, 541 g/m³, has been reported for the dibromo compound $\text{CF}_3\text{CHOHCHBr}_2$.⁶⁶

b. Toxicity. Almost no information is available; however, significant acute toxicity problems are expected. 2 hour mouse LC_{50} values of 0.38 % have been estimated by QSAR techniques for both $\text{CBrF}_2\text{CH}_2\text{OH}$ and $\text{CBrF}_2\text{CF}_2\text{CH}_2\text{OH}$.⁵⁰ The estimate for $\text{CF}_3\text{CHOHCH}_2\text{Br}$ was 0.46 % and that for $\text{CF}_3\text{CBrFCH}_2\text{OH}$ was 0.23 %. $\text{CHBrCF}_2\text{CH}_2\text{OH}$ is reported to have a minimum anesthetic concentration of 100 to 500 mg/kg and a minimum lethal concentration >400 mg/kg, with poor anesthesia.

c. Materials Compatibility. Bromine-containing alcohols are expected to be much more reactive toward metals than bromine-containing alkanes. There may be self reactions (*e.g.*, $\text{CH}_2\text{BrOH} \rightarrow \text{O}=\text{CH}_2 + \text{HBr}$ or $2\text{CH}_2\text{BrCH}_2\text{OH} \rightarrow \text{CH}_2\text{BrCH}_2\text{-O-CH}_2\text{CH}_2\text{OH} + \text{HBr}$) forming highly corrosive hydrogen bromide.

d. Colligative Properties. Some boiling points from the GlobeTech Chemical Options Database are shown in the adjacent table. Since some fluorination is required to keep the flammability down and since alcohols with fluorine atoms on the carbon attached to the hydroxyl group are unstable, bromine-containing fluoroalcohols will have to have at least two carbon atoms. The boiling points will be high.

Compound	BP (°C)
$\text{CBrF}_2\text{CH}_2\text{OH}$	67
$\text{CF}_3\text{CHOHCH}_2\text{Br}$	124
CHBrFCH(OH)CF_3	124
$\text{CHBrCF}_2\text{CH}_2\text{OH}$	149
$\text{CF}_3\text{CBrFCH}_2\text{OH}$	97
$\text{CF}_3\text{CHBrCH}_2\text{OH}$	108
$\text{CF}_3\text{CH(OH)CHBrCH}_3$	66
$\text{CF}_3\text{CBrFCH(CH}_3\text{)OH}$	112
$\text{CF}_3\text{CBrFC(CH}_3\text{)}_2\text{OH}$	128
$\text{CF}_3\text{CH(OH)CHBrCH}_2\text{CH}_3$	94
$\text{CF}_3\text{CH(OH)CBr(CH}_3\text{)CH}_3$	68
$\text{CF}_3\text{CBrClC(CH}_3\text{)}_2\text{OH}$	137
$\text{CF}_3\text{CBr}_2\text{C(CH}_3\text{)}_2\text{OH}$	152
$\text{CF}_3\text{CHOHCHBr}_2$	156
$\text{CBr}_2\text{FCH}_2\text{OH}$	85

e. Atmospheric Impact. Alcohols, even fluorine-containing alcohols, are expected to have a significant water solubility. For this reason, rainout is likely to be significant and the atmospheric lifetime small. Insufficient data are available to estimate what the ODP values might be.

f. Overall Assessment. Although bromine-containing alcohols are likely to have good environmental properties and may have good extinguishing characteristics, they may have unacceptable toxicities and compatibility properties. Nevertheless, it is recommended that some additional investigation better define the ranges of the latter properties. This should be given low priority.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied		X	
Completely unstudied			
Estimated			

3. Chlorine-containing Alcohols

In this section we consider alcohols that contain chlorine and perhaps fluorine.

a. Fire Suppression Effectiveness. No data are available. Hydrochlorofluoroalcohols are expected to extinguish flames primarily by physical cooling and to have extinguishment concentrations similar to those of the HCFCs.

b. Toxicity. The toxicities of chlorine-containing alcohols are expected to be relatively high.

c. Materials Compatibility. Chlorofluoroalcohols are expected to be more corrosive than HCFCs.

d. Colligative Properties. Since some fluorination is required to keep the flammability down and since alcohols with fluorine atoms on the carbon attached to the hydroxyl group are unstable, chlorine-containing fluoroalcohols will have to have at least two carbon atoms and will have to contain some hydrogen atoms. Due to hydrogen bonding, the boiling points will be significantly higher than the corresponding HCFCs.

e. Atmospheric Impact. Alcohols, even fluorine-containing alcohols, are expected to have a significant water solubility. For this reason, rainout is likely to be significant and the atmospheric lifetime, small. Insufficient data are available to estimate what the ODP values might be.

f. Overall Assessment. Hydrochlorofluoroalcohols are likely to have good environmental properties; however, they are likely to have unacceptable toxicities and compatibility characteristics. There is no reason to expect their extinguishment characteristics to be sufficiently good to warrant investigation.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied			
Completely unstudied	X		
Estimated			

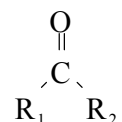
4. Fluorine-containing Alcohols

- a. Fire Suppression Effectiveness.** No data are available. Hydrofluoroalcohols are expected to extinguish flames primarily by physical cooling and to have extinguishment concentrations similar to those of the HFCs. Flammability may be of some concern; *e.g.*, CF₃CH₂OH has a flash point.⁶⁷
- b. Toxicity.** The toxicities of fluorine-containing alcohols are expected to be relatively high.
- c. Materials Compatibility.** Chlorofluoroalcohols are expected to be more corrosive than HFCs.
- d. Colligative Properties.** Since alcohols with fluorine atoms on the carbon attached to the hydroxyl group are unstable, fluoroalcohols will have to have at least two carbon atoms and will have to contain some hydrogen atoms. Due to hydrogen bonding, the boiling points will be significantly higher than the corresponding HFCs.
- e. Atmospheric Impact.** Alcohols, even fluorine-containing alcohols, are expected to have a significant water solubility. For this reason, rainout is likely to be significant and the atmospheric lifetime, short. CF₃CH₂OH has been estimated to have an atmospheric lifetime of 0.46 years based on reaction with •OH only⁶⁸ and a 100 year GWP based on CO₂ of 26.⁶²
- f. Overall Assessment.** Due to their expected high toxicities and poor extinguishment performance, there is no reason to consider these compounds further.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied			
Completely unstudied	X		
Estimated			

E. Aldehydes and Ketones

Aldehydes and ketones are saturated hydrofluorocarbons having the structure



For aldehydes, at least one of the R_n substituents is hydrogen. Ketones have only carbon atoms directly bonded to the carbonyl carbon. Carboxylic acids and their esters, which have an oxygen atom directly bonded to the carbonyl carbon are not considered here.

1. Iodine-containing Aldehydes and Ketones

a. Fire Suppression Effectiveness. No extinguishment data have been reported for iodine-containing ketones and aldehydes. Like other iodine-containing materials, however, such compounds are expected to have good extinguishment efficiency.

b. Toxicity. Lower aldehydes attack exposed moist tissue, especially eyes and mucous membranes. Higher aldehydes penetrate deeper into the respiratory tract and affect the lungs. Many members of the family are mutagens, and all have anesthetic properties. Ketones are less toxic but they can act as narcotics and as neurotoxins. The toxicities of iodine-containing ketones and aldehydes are unknown. It is expected that such compounds will be even more toxic than the parent compounds. Compounds with halogen atoms on carbon atoms alpha to the carbonyl group are often strong lachrymators.

c. Materials Compatibility. Carbonyl-containing compounds will be more corrosive than the corresponding alkanes.

d. Colligative Properties. No data are available for iodine-containing aldehydes and ketones; however, since such compounds must contain a carbonyl group and avoid halogen atoms on the alpha carbon, structural requirements indicate relatively high molecular weights.

e. Atmospheric Impact. Iodine is likely to be the controlling factor in determining the atmospheric lifetime, rather than the carbonyl group.

f. Overall Assessment. There is little to recommend this class. Iodine does not need the carbonyl functionality to effect a short atmospheric lifetime.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied			
Completely unstudied	X		
Estimated			

2. Bromine-containing Aldehydes and Ketones

a. Fire Suppression Effectiveness. No extinguishment data have been reported for bromine-containing ketones and aldehydes. Like other bromine-containing materials, however, such compounds are expected to have good extinguishment properties.

b. Toxicity. Lower aldehydes attack exposed moist tissue, especially eyes and mucous membranes. Higher aldehydes penetrate deeper into the respiratory tract and affect the lungs. Many members of the family are mutagens, and all have anesthetic properties. Ketones are less toxic but they can act as narcotics and as neurotoxins. The toxicities of bromine-containing ketones and aldehydes are unknown. It is expected that such compounds will be even more toxic than the parent compounds. Compounds with halogen atoms on carbon atoms alpha to the carbonyl group are often strong lachrymators.

c. Materials Compatibility. Carbonyl-containing compounds will undoubtedly be more corrosive than the corresponding alkanes.

d. Colligative Properties. Few data are available for bromine-containing aldehydes and ketones; however, since such compounds must contain a carbonyl group and avoid halogen atoms on the alpha carbon, structural requirements indicate relatively high molecular weights.

e. Atmospheric Impact. Carbonyl compounds can undergo photolysis and may also undergo physical removal, depending on their water solubility. Reaction with hydroxyl free radicals requires the presence of hydrogen atoms. Rate constants for reactions with hydroxyl free radicals and estimated quantum yields and absorption cross sections for photolysis indicate that aldehydes will have short atmospheric lifetimes, on the order of a few hours to approximately one month.^{69,70,71} The rate constants for reactions of non-halogenated ketones with hydroxyl free radicals are relatively large, and the atmospheric lifetimes will be on the order of days. In addition, these compounds undergo photolysis in the troposphere. The method of Wuebbles and Connell⁷² used to estimate lifetimes due to hydrogen atom abstraction, however, shows that halogen substitution greatly increases the atmospheric lifetimes. Thus, halogenated ketones are suitable only if the photolytic lifetime is sufficiently short. Without absorption cross sections for compounds of interest, photolysis estimates cannot be made.

f. Overall Assessment. Although the presence of a carbonyl group may give a sufficiently short atmospheric lifetime to allow use of the brominated compounds, the expected problems with molecular weight (high boiling points), toxicity, and, possibly compatibility cause us to recommend against investigations of this family.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied			
Completely unstudied	X		
Estimated			

3. Chlorine-containing Aldehydes and Ketones

a. Fire Suppression Effectiveness. No extinguishment data have been reported. These compounds are expected to be primarily physical extinguishants, and their effectiveness is unlikely to differ significantly from those of HCFCs of the same molecular weight.

b. Toxicity. Lower aldehydes attack exposed moist tissue, especially eyes and mucous membranes. Higher aldehydes penetrate deeper into the respiratory tract and affect the lungs. Many members of the family are mutagens, and all have anesthetic properties. Ketones are less toxic but they can act as narcotics and as neurotoxins. The toxicities of chlorine-containing ketones and aldehydes are unknown. It is expected that such compounds will be even more toxic than the parent compounds. Compounds with halogen atoms on carbon atoms alpha to the carbonyl group are often strong lachrymators.

c. Materials Compatibility. Carbonyl-containing compounds will undoubtedly be more corrosive than the corresponding HCFCs.

d. Colligative Properties. Since chlorine-containing aldehydes and ketones must contain a carbonyl group and should avoid halogen atoms on the alpha carbon, structural requirements indicate relatively high molecular weights.

e. Atmospheric Impact. Carbonyl compounds can undergo photolysis and may also undergo physical removal, depending on the water solubility. Reaction with hydroxyl free radicals requires the presence of hydrogen atoms. Rate constants for reactions with hydroxyl free radicals and estimated quantum yields and absorption cross sections for photolysis indicate that aldehydes will have short atmospheric lifetimes, on the order of a few hours to approximately one month.^{69,70,69} The rate constants for reactions of non-halogenated ketones with hydroxyl free radicals are relatively large, and the atmospheric lifetimes will be on the order of days. In addition, these compounds undergo photolysis in the troposphere. The method of Wuebbles and Connell⁷² used to estimate lifetimes due to hydrogen atom abstraction, however, shows that halogen substitution greatly increases the atmospheric lifetimes. Thus, halogenated ketones are suitable only if the photolytic lifetime is sufficiently short. Without absorption cross sections for compounds of interest, photolysis estimates cannot be made.

f. Overall Assessment. There is nothing to recommend these physical extinguishants. They are likely to be much more toxic than the HCFCs and to have materials compatibility and boiling point problems. There are better ways to decrease atmospheric lifetime than incorporation of a carbonyl group.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied			
Completely unstudied	X		
Estimated			

4. Fluorine-containing Aldehydes and Ketones

a. Fire Suppression Effectiveness. Fire suppression data are almost completely unknown for fluorinated carbonyl compounds. A major exception, however, is dodecafluoro-2-methylpentan-3-one, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$, which has a propane cup burner heptane extinguishment volume fraction of 3.5 %.⁷³ This can be compared with values of 3.6 % for halon 1211 and 4.3 % for halon 1301 with the same fuel.⁷³ Unfortunately, data for *n*-heptane extinguishment with this perfluorinated ketone have not been reported. Hexafluoroacetone, CF_3COCF_3 , has a cup burner extinguishment volume fraction of over 6 %.

b. Toxicity. Lower aldehydes attack exposed moist tissue, especially eyes and mucous membranes. Higher aldehydes penetrate deeper into the respiratory tract and affect the lungs. Many members of the family are mutagens, and all have anesthetic properties. Ketones are less toxic but they can act as narcotics and as neurotoxins. Hexafluoroacetone is known to be highly toxic; however, dodecafluoro-2-methylpentan-3-one, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$ is reported to have a relatively low toxicity. The 4 hour LC_{50} value is greater than 10 %, and the cardiac sensitization NOEL is 10 %.⁷³

c. Materials Compatibility. Carbonyl-containing compounds will undoubtedly be more corrosive than the corresponding HFCs or PFCs. The fully fluorinated compound $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$ is reported to show no reaction with a variety of metals at its boiling point.⁷³ Some results for interactions with elastomers have been reported; however, testing is still under way.⁷³

d. Colligative Properties. Since fluorine-containing aldehydes and ketones must contain a carbonyl group and should avoid halogen atoms on the alpha carbon, structural requirements indicate relatively high molecular weights compared to, *e.g.*, the HFCs. There is one fluorinated ketone reported to be a fire extinguishant, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$.

e. Atmospheric Impact. ODP is not a problem with these compounds; however, GWP values and atmospheric persistence must be considered. Carbonyl compounds can undergo photolysis and may also undergo physical removal, depending on the water solubility. Reaction with hydroxyl free radicals requires the presence of hydrogen atoms. Rate constants for reactions with hydroxyl free radicals and estimated quantum yields and absorption cross sections for photolysis indicate that aldehydes will have short atmospheric lifetimes, on the order of a few hours to approximately one month.^{69,70,69} The rate constants for reactions of non-halogenated ketones with hydroxyl free radicals are relatively large, and the atmospheric lifetimes will be on the order of days. In addition, these compounds undergo photolysis in the troposphere. The method of Wuebbles and Connell⁷² used to estimate lifetimes due to hydrogen atom abstraction, however, shows that halogen substitution greatly increases the atmospheric lifetimes. Thus, halogenated ketones may have low GWP values only if the photolytic lifetime is sufficiently short. Without absorption cross sections for compounds of interest, photolysis estimates cannot be made. $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$ is expected to have an atmospheric lifetime of 3 to 5 days and a 100 year GWP of 1 (compared to CFC-11).

f. Overall Assessment. In the absence of the recent results reported for $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$, there was little to recommend the fluorinated ketones as extinguishants. This is still true for the aldehydes; however, at least some of the fully fluorinated ketones may have acceptable environmental and toxicity characteristics. Little is known about the fire extinguishing capabilities although studies are under way.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied		X	
Completely unstudied			
Estimated			

F. Aromatics

Aromatics are resonance-stabilized cyclic compounds. Owing to molecular weight considerations, the only compounds of interest here are derivatives of benzene, C₆H₆.

1. Iodine-containing Aromatics

- a. Fire Suppression Effectiveness.** No extinguishment studies have been made for any iodine-containing aromatic. Although compounds containing iodine are usually good extinguishants, the large number of carbon atoms (at least six) may supply significant combustion energy and this may negate much of the suppression characteristics.
- b. Toxicity.** No information is available on the toxicity of iodine-containing fluoroaromatics. It is expected that such compounds will have toxicities similar to those of the iodine-containing alkanes, some of which are known to have very low cardiac sensitization levels.^{8,10}
- c. Materials Compatibility.** The materials compatibility properties are totally unknown; however, the iodine-containing aromatics are not expected to be significantly more corrosive than the iodine-containing alkanes.
- d. Colligative Properties.** The iodine-containing aromatics will have very large molecular weights and high boiling points, even when fluorinated.
- e. Atmospheric Impact.** Due to the presence of iodine, iodinated aromatics are expected to have very short atmospheric lifetimes and low GWP and ODP values.
- f. Overall Assessment.** These very large molecules carry a large fuel burden and have low vapor pressures. It is unlikely that suitable iodine-containing aromatics can be found for total flooding. In fact, the only reason to consider these compounds any further might be the slim possibility of finding a compound with low toxicity.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied			
Completely unstudied	X		
Estimated			

2. Bromine-containing Aromatics

a. Fire Suppression Effectiveness. Only one extinguishment study has been made for a bromine-containing aromatic: 1-bromo-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene (*n*-heptane cup burner, 4.26 volume percent.⁶⁴ Although compounds containing bromine are usually good extinguishants, the large number of carbon atoms (at least six) may supply significant combustion energy and this may negate much of the suppression characteristics. The compound expected to have the highest volatility, bromopentafluorobenzene, is flammable (flash point 87 °C).⁷⁴

b. Toxicity. Few data are available on bromine-containing fluoroaromatics. A 2 hour mouse LC₅₀ of 0.38 % has been estimated for bromopentafluorobenzene using QSAR methods.⁵⁰ Exposure of mice to 1.8 % to 2.4 % of this compound produced no anesthesia, and all survived. QSAR methods have also been used to estimate a 2 hour mouse LC₅₀ of 0.5 % for 2-bromoheptafluorotoluene, 0.4 % for 3-bromoheptafluorotoluene, and 0.4 % for 4-bromoheptafluorotoluene.⁵⁰

c. Materials Compatibility. The materials compatibility properties are totally unknown; however, the bromine-containing aromatics are not expected to be significantly more corrosive than the bromine-containing alkanes.

d. Colligative Properties. The boiling points for bromine-containing aromatics are very high. It is very unlikely that such agents could be used in total flooding applications, and the volatility may be too low even for streaming.

Compound	Formula	BP (°C)	Ref.
Bromopentafluorobenzene	C ₆ BrF ₅	134	75
2-bromoheptafluorotoluene	C ₆ BrF ₄ CF ₃	154	76
3-bromoheptafluorotoluene	C ₆ BrF ₄ CF ₃	153	77
4-bromoheptafluorotoluene	C ₆ BrF ₄ CF ₃	152	78

e. Atmospheric Impact. Like the alkenes, hydroxyl free radicals can add to aromatics. At about room temperature most •OH radical reactions studied to date proceed by addition to the aromatic ring rather than by abstraction of a hydrogen atom. Rate constants for the reaction of hydroxyl free radicals with aromatic compounds are similar to those observed for the alkenes.⁷⁹ Of particular interest is the 298 K rate constant of $k_{OH} = 2.2 \times 10^{-13} \text{ cm}^3/\text{molecule-s}$ and approximately $3 \times 10^{-12} \text{ cm}^3/\text{molecule-s}$ observed for reactions with hexafluorobenzene (C₆F₆) and *n*-propylpentafluorobenzene (CH₃CH₂CH₂C₆F₅), respectively.⁸⁰ The reaction rates for the nonfluorinated analogs are somewhat faster: $k_{OH} = 1.59 \times 10^{-12}$ for benzene and $7.8 \times 10^{-12} \text{ cm}^3/\text{molecule-s}$ for *n*-propylbenzene.⁸⁰ Thus, fluorination of the aromatic ring decreases the reaction rate with •OH. One can calculate the first order rate constants for the two fluorinated compounds as $k_1 = k_{OH} [\bullet\text{OH}]$. This gives $k_1 = 2.1 \times 10^{-7} \text{ s}^{-1}$ ($t_{1/e} = 1/k_1 = 54$ days) for hexafluorobenzene and $k_1 = 2.9 \times 10^{-6} \text{ s}^{-1}$ ($t_{1/e} = 1/k_1 = 4$ days) for *n*-propylpentafluorobenzene.

One can use the method of Wuebbles and Connell⁷² to estimate first-order rate constants and atmospheric lifetimes for a series of aromatic compounds of interest. The estimation method gives $k_1 = 8 \times 10^{-8} \text{ s}^{-1}$, ($t_{1/e} = 145$ days) for hexafluorobenzene and $k_1 = 3 \times 10^{-7} \text{ s}^{-1}$, ($t_{1/e} = 39$ days) for *n*-propylpentafluorobenzene. These rate constants are a little smaller than those determined from the experimental second-order rate constants above. These values indicate that aromatics have an excellent potential for environmental acceptability, even with bromine present.

f. Overall Assessment. Despite the possibly good environmental characteristics, the exceedingly high molecular weights and fuel burden mitigate against further study of these compounds.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied			
Completely unstudied	X		
Estimated			

3. Chlorine-containing Aromatics

a. Fire Suppression Effectiveness. *N*-heptane cup burner extinguishment volume fractions have been reported⁴ for 1,3-dichlorotetrafluorobenzene (6 %, 537 g/m³) and chloropentafluorobenzene (5.4 %, 447 g/m³). Much of this effectiveness is due to the large heat capacities of these heavy compounds.

b. Toxicity. Some chlorine-containing aromatics are known to be carcinogens (*e.g.*, chlorobenzene, 1,4-dichlorobenzene, hexachlorobenzene); however, no toxicity data are available for chlorine-containing fluoroaromatics. There is little reason to believe that such compounds would have exceptionally high acute toxicities.

c. Materials Compatibility. The materials compatibility properties are totally unknown; however, the chlorine-containing aromatics are not expected to be significantly more corrosive than the bromine-containing alkanes.

d. Colligative Properties. The chlorinated aromatics are expected to have high boiling points and low volatilities, even when fluorinated. 1,3-Dichlorotetrafluorobenzene has a boiling point of 151 °C and a melting point of 73 °C.⁸¹ The normal boiling point of chloropentafluorobenzene is 117 °C.

e. Atmospheric Impact. As with the bromine-containing aromatics, hydroxyl free radicals can add to these compounds, resulting in atmospheric lifetimes possibly within an acceptable range.

f. Overall Assessment. Despite the possibly good environmental characteristics, the high molecular weights and fuel burdens mitigate against further study of these compounds. Besides, these compounds are not expected to be particularly outstanding fire suppressants.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied	X		
Completely unstudied			
Estimated			

4. Fluorine-containing Aromatics

a. Fire Suppression Effectiveness. No fire suppression testing has been carried out on fluorine-containing aromatics; however, there is no reason to believe that these compounds will behave any different than other higher molecular weight physical agents. The large number of carbon bonds available upon reaction supply significant energy, which will negate in very large part the suppression effects. Pentafluorobenzene (C_6HF_5) and perfluorotoluene ($C_6F_5CF_3$) are flammable in air.

b. Toxicity. Some toxicity data are available for trifluoromethyl-substituted benzenes, which are being considered as solvents. All mice died in 6 hours after 10 min exposure to a volume fraction of 0.5 % to 0.9 % of (trifluoromethyl)pentafluorobenzene; pentafluorobenzene produced anesthesia in mice with all surviving.⁴³

c. Materials Compatibility. The materials compatibility properties are unknown; however, the fluorine-containing aromatics are not expected to have compatibility problems.

d. Colligative Properties. The boiling points are 85 °C for pentafluorobenzene and 103 °C for perfluorotoluene.⁴³ (Trifluoromethyl)benzene has a boiling point of 104 °C.⁸²

e. Atmospheric Impact. These compounds have zero ODP values. As with the iodine- and bromine-containing aromatics, hydroxyl free radicals can add to these compounds, resulting in atmospheric lifetimes that would mitigate any global warming contribution.

f. Overall Assessment. Despite the possibly good environmental characteristics, the high molecular weights and fuel burdens mitigate against further study of these compounds. Besides, these compounds are not expected to be particularly outstanding fire suppressants.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied			
Completely unstudied	X		
Estimated			

III. Nitrogen-containing Compounds

A. Nitriles

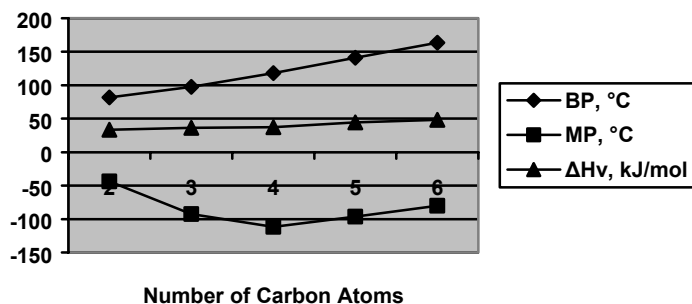
Nitriles are organic compounds containing the $-C\equiv N$ group.

a. Fire Suppression Effectiveness. No fire suppression tests have been conducted on nitrile compounds, and there is no evidence or reason to believe that the nitrile group itself possesses an intrinsic fire suppression capability. Nonhalogenated nitriles are known or are expected to be flammable. Fluorination may well reduce this, and the resulting compounds would act mainly as physical suppressants. The addition of bromine or iodine would impart chemical flame inhibition to nitriles.

b. Toxicity. Most nitriles are moderately to highly toxic. Propionitrile is quite toxic, apparently through metabolism of the cyanide ion. One-third of rats exposed to a volume fraction of 0.05 % (500 ppm by volume) of propionitrile in air died.⁸³ Similarly, butyronitrile and isobutyronitrile are highly toxic by skin contact or inhalation.^{84,85} There are no published data on the highly fluorinated nitriles or nitriles containing bromine or iodine.

c. Materials Compatibility. Nitriles are not inherently highly corrosive toward metals. They do attack some polymeric materials. Nitriles are slowly hydrolyzed, particularly in the presence of acids or bases, to give carboxylic acids and ammonia; however, the net change in pH (indicative of corrosive tendencies) is nominally zero since both a weak base and a weak acid are formed.

d. Colligative Properties. The following graph shows the variation of boiling point, melting point and heat of vaporization (at or near 25 °C) for linear nitriles containing 2 through 6 carbon atoms.⁸⁶ The simplest nitrile, acetonitrile (methyl cyanide) has a boiling point of 81.6 °C and other nitriles have higher boiling points. The freezing points for compounds up to 6 carbon atoms are all below 80 °C except for acetonitrile, which is -43.8 °C. Halogenation is expected to cause significant property changes. For example, trifluoroacetonitrile has a surprisingly low boiling point of -64 °C.⁸⁷



e. Atmospheric Impact. Nonhalogenated nitriles have no intrinsic ODP, and no estimate has been made of their GWP values; however, consideration of atmospheric chemistry (see below) indicates that GWPs should be negligible (assuming relatively rapid removal by rainout). Halogenated nitriles, however, could have significant ODP values and GWP values, depending on the degree of halogenation and the type of halogen atoms present.

The approximate rate constant for reaction of $\bullet OH$ with acetonitrile at 298 K is $2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (recommended, estimated uncertainty $\pm 40\%$) and with propionitrile is $19 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.⁷⁹

These compare with recommended values of $0.84 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for methane and $26.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for ethane, both at 298 K. Thus, the presence of a nitrogen atom in the nitriles does not appear to increase the reaction rate with $\bullet\text{OH}$ (compared with alkanes) significantly. Using a globally averaged $\bullet\text{OH}$ concentration of $9.7 \times 10^5 \text{ molecule/cm}^3$ ⁸⁸, one calculates an estimated lifetime for acetonitrile (three hydrogen atoms) based only on reaction with $\bullet\text{OH}$ of 1.53 years and for propionitrile (5 hydrogen atoms) of approximately 2 months.

The polarity induced by nitrogen causes nitriles to be completely (*e.g.*, acetonitrile) or somewhat (*e.g.*, propionitrile) water soluble. This greatly increases the probability for relatively rapid removal by rainout. Some atmospheric hydrolysis could also occur. This is expected to be negligible for homogeneous gas phase reactions, but could occur heterogeneously on atmospheric water droplets.

The addition of fluorine atoms to decrease flammability will decrease the reaction rates with $\bullet\text{OH}$ and will also decrease the water solubility, both changes increasing the atmospheric lifetime.

f. Overall Assessment. It appears unlikely that a nitrile could be designed to have desirable values of all the needed properties. However, it is suggested that a cursory examination of the possibility for inherent fire suppression capability of the nitrile group (possibly using CF_3CN) be pursued. A positive result might stimulate a closer look at this family.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied			
Completely unstudied		X	
Estimated			

B. Nitro Compounds

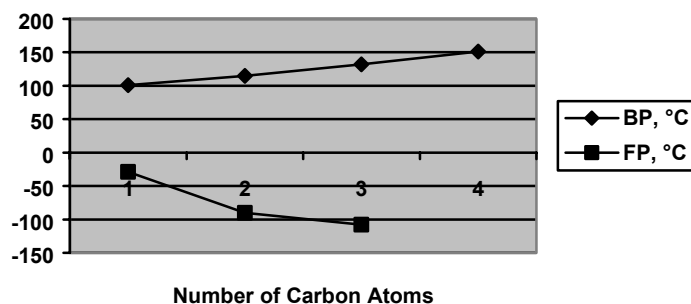
Nitro compounds contain the $-\text{NO}_2$ group. The simplest nitro compound is nitromethane (CH_3NO_2).

a. Fire Suppression Effectiveness. Nitro compounds are often dangerously flammable and/or explosive. As a result, no fire suppression tests have been conducted using nitro compounds, and there is no evidence or reason to believe that the nitrile group itself possesses an intrinsic fire suppression capability.

b. Toxicity. Most nitro compounds are highly toxic.

c. Materials Compatibility. Nitro compounds generally have some materials compatibility problems.

d. Colligative Properties. The following graph shows the variation of boiling point and freezing point (not melting point) for linear nitroalkanes containing 1 through 4 carbon atoms (nitro group on the first carbon atom in the butane and propane derivatives). The boiling points are high, in all cases over $100\text{ }^\circ\text{C}$. Fluorination would be expected to lower these boiling points.



e. Atmospheric Impact. Nitromethane reacts with $\bullet\text{OH}$ slightly faster than methane ($1.58 \times 10^{-14}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ versus $0.84 \times 10^{-14}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ at 298 K) and nitroethane reacts slightly slower than ethane ($7.2 \times 10^{-14}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ versus $27 \times 10^{-14}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ at 298 K).⁸⁹ The differences are negligible, and nitroalkanes are expected to have atmospheric lifetimes similar to those of the hydrocarbons. Nitro compounds have no intrinsic ODP.

f. Overall Assessment. Owing to the physical, toxicological, stability, and flammability problems of nitro compounds, examination of this group for fire suppression is not recommended.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied			
Completely unstudied	X		
Estimated			

C. Organic Nitrates and Nitrites

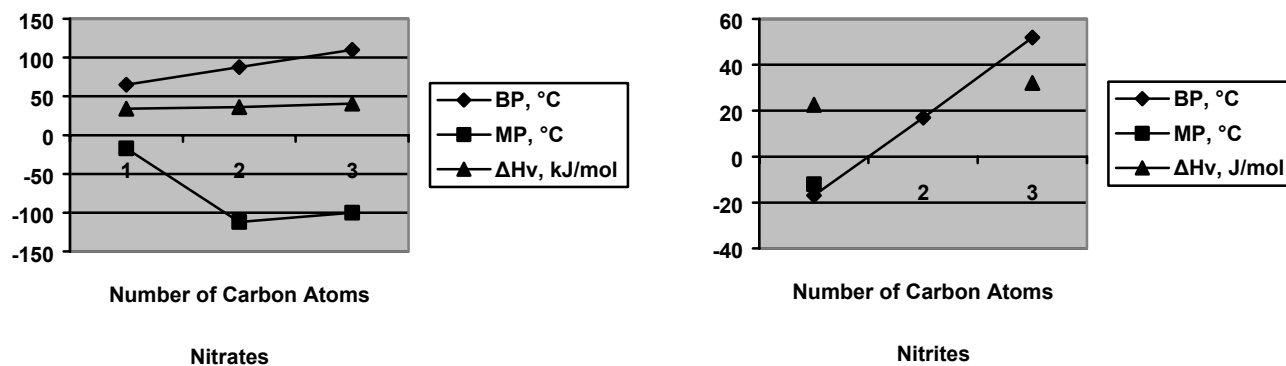
Organic nitrates and nitrites are compounds containing, respectively, the groups $-\text{ONO}_2$ and $-\text{ONO}$. The simplest organic nitrates and nitrites are methyl nitrate (CH_3ONO_2) and methyl nitrite (CH_3ONO).

a. Fire Suppression Effectiveness. The combustion properties of nitrates and nitrites are fairly well known, primarily because both types of compounds are often explosive. No fire suppression tests have been conducted using nitrates and nitrites, and there is no evidence or reason to believe that these groups possess any intrinsic fire suppression capability. It is not clear whether the addition of bromine or iodine would be sufficient to stifle the explosive tendencies.

b. Toxicity. Nitrates and nitrites have relatively high toxicities. In the case of nitrates, methemoglobin formation is the primary toxicity cause. Nitrites are also known to induce methemoglobin formation and, have even caused human death by this route.⁹⁰ (Methemoglobin is the oxidized form of hemoglobin in which the iron in the heme component has been oxidized from the ferrous (+2) to the ferric (+3) state. This renders the hemoglobin molecule incapable of effectively transporting and releasing oxygen to the tissues.) A 4 hour LC_{50} of 0.13 % has been reported for rats.⁹¹

c. Materials Compatibility. To date, no information has been obtained on general materials compatibilities of nitrates and nitrites.

d. Colligative Properties. The following graphs show the variation of boiling point, melting point and heat of vaporization for some nitrates and nitrites with 1 through 3 carbon atoms. (These data are from a variety of sources, but primarily from the NIST Chemistry WebBook.) The boiling point data are very uncertain due to the instability of the nitrates and nitrites.



e. Atmospheric Impact. Nonhalogenated nitrites and nitrates have no intrinsic ODP, and no estimate has been made of the GWP values. Halogenated nitriles, however, could have significant ODP values and GWP values, depending on the degree of halogenation and the type of halogen atoms present.

A relatively large amount of data has been reported for reaction of nitrates and nitrites with $\bullet\text{OH}$.⁷⁹ The approximate rate constant at or near 298K for reaction with $\bullet\text{OH}$ is $3.4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for methyl nitrate, $49 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for ethyl nitrate, and $62 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for propyl nitrate. Similarly, the approximate rate constant at or near 298 K for reaction with $\bullet\text{OH}$ is $12 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for methyl nitrite (large unexplained experimental variation), $177 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for ethyl nitrite, and $235 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for propyl nitrite. These can be compared with recommended values of $0.84 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for methane, $27 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for ethane, and $115 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ all at 298 K. Thus, the nitrates and especially the nitrites have

reaction rates with •OH somewhat higher than those of the corresponding alkanes. Using a globally averaged •OH concentration of 9.7×10^5 molecule/cm³⁸⁸, one calculates estimated lifetimes for methyl nitrate, ethyl nitrate, and propyl nitrate of, respectively, 1 year, 24 days, and 19 days. For methyl nitrite, ethyl nitrite, and propyl nitrite the values are 3 months, 7 days, and 5 days. The addition of halogen atoms, such as fluorine, will decrease the reaction rates with •OH.

The nitrates and nitrites are slightly water soluble, a property that increases the probability for removal by rainout.

f. Overall Assessment. While the nitrates and nitrites are expected to have low atmospheric lifetimes, the absence of any proven inherent fire suppression capabilities due to the nitrate and nitrite groups, the high toxicity, and, in particular, the explosive tendencies makes these compounds unacceptable for study.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied			
Completely unstudied	X		
Estimated			

D. Nitroso Compounds

Nitroso compounds are organics containing the -NO group. The simplest nitrosoalkane is nitrosomethane (CH₃NO); the simplest nitrosoarene is nitrosobenzene (C₆H₅NO).

a. Fire Suppression Effectiveness. No fire suppression tests have been conducted on nitroso compounds, and there is no evidence or any reason to believe that the nitroso group itself possesses an intrinsic fire suppression capability. Bromination would probably be required to produce an inhibitor. Some nitroso compounds (*e.g.*, 4-nitrosophenol) are explosive.

b. Toxicity. Little is known of the toxicity of the nitrosoalkanes; however, these can react to form N-nitroso compounds, which are known to be strong carcinogens. A range of toxicities has been reported for the nitrosoarenes.

c. Materials Compatibility. No information is available.

d. Colligative Properties. No information is available for the nitrosoalkanes, but they are unstable, tending to rearrange, oxidize, and dimerize. The nitrosoarenes are solids at room temperature.

e. Atmospheric Impact. Nonhalogenated nitriles have no intrinsic ODP, and no estimate has been made of the GWPs. No lifetimes or rate constants for atmospheric reactions have been reported.

f. Overall Assessment. In view of the stability and toxicity problems associated with nitroso compounds, no further study is recommended.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied			
Completely unstudied	X		
Estimated			

E. Fluoroalkyl Amines

Amines are derivatives of ammonia (NH_3) and have the general formula $\text{NRR}'\text{R}''$ where at least one of the nitrogen substituents is an alkyl group. The others can be hydrogen atoms. 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.

a. Fire Suppression Effectiveness. Research from the National Industrial Research Institute of Nagoya has focused on fluoroalkylamines, with an emphasis on perfluoroalkyl derivatives, as fire suppressants.⁹² The inhibition effect of several bromine-free polyfluoroalkylamines including $\text{N}(\text{CF}_3\text{CF}_2)_3$, $\text{N}(\text{CF}_3)_2(\text{CF}_2\text{CF}_3)$, $\text{N}(\text{CF}_3)_2(\text{CF}_2\text{CHF}_2)$, and $\text{N}(\text{CF}_3)_2(\text{CF}=\text{CF}_2)$ on flame propagation has been measured by determining the laminar burning velocity for a mixture of 9.5 % methane, 90.0 % air, and 0.5 % inhibitor, at an initial temperature of 298 K and a pressure of 101 kPa. All of the fluoroalkylamines inhibited flame propagation less efficiently than CF_3Br , but more efficiently than HFC-227ea ($\text{CH}_3\text{CHF}_2\text{CF}_3$). Calculations showed that the inhibition effect of the fluoroalkylamines was caused not only by physical factors, but also by a chemical process in which fluorinated species capture combustion chain carriers ($\bullet\text{H}$, $\bullet\text{O}$, and $\bullet\text{OH}$) to form stable HF molecules. The inhibition efficiencies of fluoroalkylamines were found to be higher than those of fluoroalkanes since fluoroalkylamine decomposes to reactive fluoroalkyl radicals in the lower temperature region of each flame.⁹³ *Ab initio* molecular orbital calculations indicate that fire suppression by perfluoromethylamines is due, in part, to reactions of the trifluoromethyl radical, which can be easily released from perfluoroalkyl-amine by dissociation of C-N bonds.⁹⁴ Others had previously found that CF_3 acts as a chemical inhibitor.³⁰

b. Toxicity. Amines with at least partially fluorinated alkyl groups are the most likely to be considered as fire extinguishants. Fluorination will lower or eliminate flammability and is likely to decrease toxicity by decreasing polarity. Some extremely limited toxicity data have been reported for partially fluorinated amines.⁶² The LC_{LO} for mouse inhalation has been reported as 500 mg/m^3 for 2,2,2-trifluoroethylamine, $(\text{CF}_3\text{CH}_2)\text{NH}_2$.²⁷ Some genotoxicity and cytotoxicity testing has been carried out on fluorinated amines using Chinese hamster lung cell cultures.⁹⁵

c. Materials Compatibility. The perfluorinated amines are known to have excellent material compatibility. Some of the higher molecular weight perfluoroamines have been used as inert fluids in electronics testing. The more highly polar less fluorinated amines are known to attack metals.

d. Colligative Properties. The following table gives the boiling points for some fluorinated amines^{62,96} The following ΔH_v values have been reported for fluorinated amines: 25.1 kJ/mol for $\text{N}(\text{CF}_3)_3$ ¹⁸, 48 kJ/mol for $\text{N}(\text{C}_4\text{F}_9)_3$ ⁹⁷, 55 kJ/mol for $\text{N}(\text{C}_5\text{F}_{11})_3$ ⁹⁷, 63 kJ/mol for $(\text{C}_3\text{F}_7)_2\text{NC}_6\text{F}_{12}\text{N}(\text{C}_3\text{F}_7)_2$ ⁹⁷, and 27 kJ/mol for $\text{N}(\text{CF}_3)_2(\text{CH}_2\text{CH}_3)$ ⁹⁸, all at the boiling point except for the last compound, where the conditions were not reported.

Compound	Boiling Point (°C)
N(CF ₃) ₃	-10
(CF ₃) ₂ NCH ₃	11-12
(CF ₃) ₂ NCF ₂ CF ₃	20.5
(CF ₃) ₂ NCH ₂ CH ₃	33-34
(CF ₃) ₂ NCH ₂ CH ₃	33.3
(CF ₃) ₂ NCH ₂ CF ₃	38
N(CF ₃)(CF ₂ CF ₃) ₂	46
(CF ₃) ₂ NCH ₂ CF ₂ H	50-52
(CH ₃) ₂ NCH ₂ CF ₃	51.35
N(CF ₂ CF ₃) ₃	70.3

e. Atmospheric Impact. A thorough assessment of the atmospheric impact of fluorinated amines and of bromofluoroamines (based on estimations and calculations) has been presented.⁶⁰ For example, the compound (CBrF₂)(CF₃)NCH₃ is estimated to have an atmospheric lifetime of 0.028 years (10 days) and an ODP of 0.006 relative to CFC-11.⁶⁰

f. Overall Assessment. Fluoroamines and bromofluoroamines are undoubtedly the most promising of the nitrogen-containing compounds as potential halon replacements. There is evidence that some could have low atmospheric lifetime, low toxicity, and good fire extinguishment capability.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied			X
Completely unstudied			
Estimated			

IV. Sulfur-containing Compounds

A. Hexacoordinate Sulfur

a. Fire Suppression Effectiveness. Cup burner results³⁰ indicate that sulfur makes little if any chemical contribution to suppression by these compounds, a conclusions reached by others specifically for SF₆.^{99,100} Note, however, that a sulfur dioxide cycle has been proposed to *inhibit* combustion by removal of hydrogen atoms.¹⁰¹ Except for the brominated derivative, none of the compounds in this table exhibit a flame suppression capability approaching that of halon 1301.

Compound	Ext. Volume Fraction (%)
SF ₆	11
SF ₅ Br	4.2
SF ₅ Cl	13
SF ₅ SF ₅	11

b. Toxicity. SF₆ has an exceedingly low toxicity; however, the closely related compound S₂F₁₀ is highly toxic. Of considerable concern is the toxicity of combustion products, such as SO₂, that could form during fire extinguishment.

c. Materials Compatibility. SF₆ is quite inert and has had extensive use as a dielectric fluid. Too little work has been performed on the derivatives to estimate their materials compatibility.

d. Colligative Properties. The data in the following table^{15,18,24,47} indicate that the properties of SF₅X compounds are in the region needed as halon 1301 substitutes.

Compound	BP (°C)	MP (°C)	ΔH _v , kJ/mol
SF ₆	-63.8 (subl)	-50.7 (triple pt.)	
SF ₅ Br	3.1		24 (est)
SF ₅ Cl	-21		21.7
SF ₅ SF ₅	30	-52.7	
SF ₅ (CF ₃)	-21		

e. Atmospheric Impact. SF₆ has a very long atmospheric lifetime of 3200 years and a calculated 100 year GWP of 13,900 compared to CO₂.⁴⁶ The lifetime and GWP of SF₅(CF₃) have been estimated as 1000 years and 6741 compared to CO₂⁶²; however, the method for making these estimations was not reported.

f. Overall Assessment. Hexavalent sulfur has no significant chemical suppression contribution, nor does it lead to improved atmospheric environmental properties. Thus, no further study is recommended.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied	X		
Completely unstudied			
Estimated			

B. Sulfides and Mercaptans

Sulfides and mercaptans contain divalent sulfur not attached to an oxygen atom: R_1-S-R_2 and $R-S-H$.

a. Fire Suppression Effectiveness. Since the nonhalogenated compounds are generally flammable, only the highly halogenated compounds are of interest. No fire suppression tests have been conducted on these, and there is no evidence indicating that the -S- group itself possesses an intrinsic chemical fire suppression capability. A sulfur dioxide cycle has been proposed to *inhibit* combustion by removal of hydrogen atoms.¹⁰¹ Added bromine or iodine would impart chemical flame suppression effectiveness.

b. Toxicity. Most organic sulfides are toxic. Moreover, chlorine substitution in the beta position can give rise to highly toxic sulfur mustards (e.g., $ClCH_2CH_2-S-CH_2CH_2Cl$). No evidence of a similar toxicity with fluorine substituents has been reported. The mercaptans tend to be highly reactive.

c. Materials Compatibility. Sulfides and particularly mercaptans are generally reactive toward metals, particularly copper and copper alloys.

d. Colligative Properties. The following table includes some boiling points and heats of vaporization.^{102,103} Of particular interest is the decrease in boiling point with fluorination.

Compound	Boiling point (°C)	ΔH_v (kJ/mol)
CH_3-S-CH_3	37.5	
CF_3-S-CF_3	-22	
$CF_3-S-C_2F_5$	6.3	28.8
$CF_3-S-C_3F_7$	38.6	27.7

e. Atmospheric Impact. Nonhalogenated sulfides have no intrinsic ODP, and no estimate has been made of the GWP values. A significant amount of kinetic data are available for reactions of sulfides and mercaptans with $\bullet OH$ ⁷⁹; however, no kinetic information is available for halogen-containing derivatives. The recommended rate constant for reaction of $\bullet OH$ with dimethyl sulfide is $460 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. The value for ethane is $27 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Thus, the presence of a sulfide atom appears to increase the reaction rate with $\bullet OH$ significantly. Using a globally averaged $\bullet OH$ concentration of $9.7 \times 10^5 \text{ molecule/cm}^3$ ⁸⁸, one calculates an estimated lifetime for dimethyl sulfide based only on reaction with $\bullet OH$ of 2.6 days. Higher molecular weight sulfides with more hydrogen atoms have larger rate constants with $\bullet OH$ and even lower atmospheric lifetimes. Thus, the sulfides appear to have intrinsically short atmospheric lifetimes. Halogenation will decrease the reaction rates owing primarily to removal of hydrogen atoms.

f. Overall Assessment. The sulfides suffer from several drawbacks: no distinctive fire suppression efficiency and potential toxicity, reactivity, and materials compatibility problems. However, the possibility that atmospheric lifetimes could be very short for brominated compounds makes a screening study of the smaller bromofluorosulfides desirable.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied			
Completely unstudied		Limited screening	
Estimated			

C. Difluorosulfur Compounds

These compounds contain tetravalent sulfur, with two of the bound ligands being fluorine atoms and the other two being partially halogenated alkyl groups.

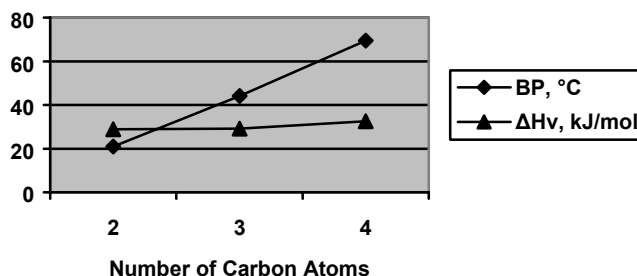
a. Fire Suppression Effectiveness. No flame suppression tests have been conducted on these tetravalent analogs of the sulfides. The expectations for suppression effectiveness are similar.

b. Toxicity. The toxicity of these compounds is unknown; however, fluorine on a sulfur(IV) compound may be highly labile. In particular, the compounds may undergo hydrolysis.

c. Materials Compatibility. Materials compatibility is unknown. If the compounds do hydrolyze, metal corrosion is probable.

d. Colligative Properties. The boiling points and heats of vaporization for a series of perfluorinated compounds are shown in the following table and graph.¹⁰² All but the lowest boiling points are higher than optimum for halon 1301 substitutes.

Compound	Boiling point (°C)	ΔH_v (kJ/mol)
$\text{CF}_3\text{SF}_2\text{CF}_3$	21	28.8
$\text{CF}_3\text{SF}_2\text{C}_2\text{F}_5$	44.1	29.2
$\text{CF}_3\text{SF}_2\text{C}_3\text{F}_7$	69.3	32.8
$\text{C}_2\text{F}_5\text{SF}_2\text{C}_2\text{F}_5$	69.5	32.2



e. Atmospheric Impact. No information is available on the lifetime or GWP for compounds of this type. Such compounds are expected to have no ODP in the absence of chlorine or bromine substitution.

f. Overall Assessment. These sulfur(IV) compounds are likely to undergo hydrolysis giving rise to toxicity and materials compatibility problems. In the absence of information showing that this is not the case, it is recommended that no future studies of these compounds be carried out.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied			
Completely unstudied	X		
Estimated			

D. Sulfoxides

These compounds contain tetravalent sulfur, with a double-bonded oxygen atom and two partially halogenated alkyl groups.

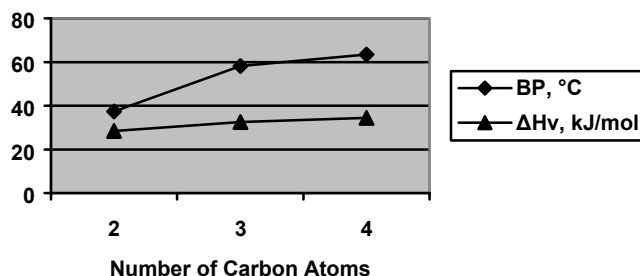
a. Fire Suppression Effectiveness. No fire suppression tests have been conducted on sulfoxides. Though there is little reason to believe that sulfur possesses an inherent extinguishing ability, a sulfur dioxide cycle has been proposed to inhibit combustion by removal of hydrogen atoms.¹⁰¹

b. Toxicity. Extensive toxicological studies have been made on dimethylsulfoxide (DMSO), the simplest of the sulfoxide compounds and a widely used solvent. DMSO is one of the least toxic organic chemicals known. Its measured LD₅₀ values (oral, dermal, and inhalation) show it to have a much lower acute toxicity than ethanol, acetone, and other common solvents. DMSO, however, does have the unique ability to penetrate human skin and this is some cause for concern.

c. Materials Compatibility. Dimethylsulfoxide is known to attack most polymers; however, it has a relatively good compatibility with metals. Similar characteristics are expected for other sulfoxides. No compatibility studies have been carried out with the fluorinated sulfoxides.

d. Colligative Properties. The boiling points and heats of vaporization for a series of perfluorinated sulfoxides are shown in the adjacent table and graph.¹⁰² As a whole, the boiling points are higher than desired for total flooding halon substitutes.

Compound	Boiling Point (°C)	ΔH_v (kJ/mol)
CF ₃ S(O)CF ₃	37.3	28.4
CF ₃ S(O)C ₂ F ₅	58.2	32.5
CF ₃ S(O)C ₃ F ₇	64	33.6
C ₂ F ₅ S(O)C ₂ F ₅	62.7	35.1



e. Atmospheric Impact. No information is available on the atmospheric lifetime or GWP values for sulfoxides. Such compounds are expected to have no ODP in the absence of chlorine or bromine substitution.

f. Overall Assessment. There is insufficient information to make a truly informed judgment on the applicability of sulfoxides as halon 1301 substitutes. It is almost certain that bromination would be needed to prepare an acceptable extinguishant. It is recommended that a screening investigation be conducted.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied			
Completely unstudied		Limited screening	
Estimated			

V. Phosphorus Compounds

A. Phosphorus Acids and Esters

Phosphorus forms a very large number of acids and esters with a rather complicated chemistry. The primary single-phosphorus oxyacids of phosphorus are phosphoric acid, $\text{OP}(\text{OH})_3$ (also known as orthophosphoric acid); phosphonic acid, $\text{OPH}(\text{OH})_2$ (originally called phosphorous acid, a name now reserved for the hypothetical acid $\text{P}(\text{OH})_3$); and phosphinic acid, $\text{OPH}_2(\text{OH})$ (originally called hypophosphorous acid, a name now used for the hypothetical alternative structure $\text{PH}(\text{OH})_2$). Phosphoric acid is triprotic, phosphonic acid is diprotic, and hypophosphonic acid is monoprotic. Phosphoric acid forms three phosphate esters: $\text{O}=\text{P}(\text{OH})_2(\text{OR})$, $\text{O}=\text{P}(\text{OH})(\text{OR})_2$, and $\text{O}=\text{P}(\text{OR})_3$. Phosphonic acid gives two phosphonate esters: $\text{O}=\text{PH}(\text{OH})(\text{OR})$ and $\text{O}=\text{PH}(\text{OR})_2$. These are often written as the “phosphite” forms $\text{P}(\text{OH})_2(\text{OR})$ and $\text{P}(\text{OH})(\text{OR})_2$, where they can be considered as derivatives of the hypothetical phosphorous acid, $\text{P}(\text{OH})_3$; however, these two esters almost certainly exist only in the phosphonate forms with $\text{P}=\text{O}$ and $\text{P}-\text{H}$ bonds. A series of very common compounds includes the trialkyl and triaryl “phosphites.” These materials appear to exist as two interconvertible forms: $\text{P}(\text{OR})_3$, which can be considered as derived from the hypothetical acid $\text{P}(\text{OH})_3$, and $\text{O}=\text{PR}(\text{OR})_2$, which can be considered as derived from phosphonic acid. In most cases, the stable compounds have the phosphonate structure with a $\text{P}=\text{O}$ bond. For historical reasons, however, the compounds are still most often named as phosphites and given the structure $\text{P}(\text{OR})_3$ rather than being named as phosphonates, with the structure $\text{O}=\text{PR}(\text{OR})_2$.

a. Fire Suppression Effectiveness. A significant amount of flame suppression testing has been carried out on a few esters of phosphorus-containing acids.^{104,105} Trimethyl phosphate ($\text{O}=\text{P}(\text{OCH}_3)_3$) shows a more pronounced effect on flame velocity than Cl_2 and Br_2 .¹⁰⁶ Phosphate esters are of particular interest as fire suppressants since they are difficult to ignite and will self-extinguish.¹⁰⁷ Dimethyl methylphosphonate (DMMP, $\text{O}=\text{P}(\text{CH}_3)(\text{OCH}_3)_2$) is approximately 40 times more effective than nitrogen on a molar basis, and about 4 times more effective than halon 1301 at suppressing opposed flow diffusion flames.¹⁰⁸ It has been concluded that phosphorus-containing compounds are more efficient flame inhibitors than CF_3Br , with the inhibition determined by the phosphorus content.¹⁰⁹ However, in suppressing cup burner flames, DMMP appears to be no more effective than CO_2 on a mass basis.¹¹⁰

b. Toxicity. The toxicities of the acids of phosphorus and their esters are highly variable. Nevertheless, this family of compounds generally has, on an average, a moderately low toxicity, at least for those compounds containing non-halogenated alkyl groups. The combustion products will include the phosphorus acids.

c. Materials Compatibility. In the absence of hydrolysis, the phosphate esters have relatively good materials compatibility. The free acids will attack metals.

d. Colligative Properties. Acids of phosphorus and their esters have low, often unacceptably low, volatilities and high boiling points. Some examples are given in the following table.¹⁵ It is anticipated that fluorination may help somewhat: $\text{P}(\text{OCH}_2\text{CF}_3)_3$ has a boiling point of 131 °C compared with 156.5 °C for the non-fluorinated compound. Additional fluorination is expected to further decrease the boiling point and increase the volatility.

Compound	Formula	Boiling Point, °C
Dimethyl methylphosphonate	O=P(CH ₃)(OCH ₃) ₂	181
Trimethylphosphite	P(OCH ₃) ₃	111.5
diethyl methylphosphonate	O=P(C ₂ H ₅)(OCH ₃) ₂	194
diethyl ethylphosphonate	O=P(C ₂ H ₅)(OC ₂ H ₅) ₂	198
Triethylphosphite	P(OC ₂ H ₅) ₃	157.9

e. Atmospheric Impact. Some phosphorus compounds are known to be ozone depleters if released in the stratosphere. Moreover, stratospheric (and tropospheric) removal reactions of phosphorus are relatively unknown. One can propose reactions such as $PO + O_3 \rightarrow PO_2 + O_2$ coupled with $PO_2 + O \rightarrow PO + O_2$ that could deplete ozone. Nevertheless, it seems unlikely that phosphorus compounds would have any global environmental impact.

f. Overall Assessment. Phosphorus compounds are highly effective at suppressing some types of flames, yet poor at suppressing others. Most work to date has emphasized alkyl phosphonates and related materials or phosphonitriles. Low volatility remains one of the major problems with phosphorus compounds as flame suppressants. Phosphorus compounds containing fluoroalkyl and hydrofluoroalkyl groups, however, are often nonflammable and have higher volatilities; they should be given high priority for additional study.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied			X
Completely unstudied			
Estimated			

B. Phosphonitriles

Phosphonitriles are compounds, possibly cyclic, containing the -P=N- unit. A common example is $P_3N_3Cl_6$.

a. Fire Suppression Effectiveness. As shown in the following table, attractively low cup burner flame extinguishment concentrations have been found for several phosphonitriles.¹⁰⁴ 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 shown very good extinguishments characteristics.¹¹¹

Compound	Ext. Vol. Fraction (%)
$P_3N_3F_6$	1.08 ± 0.07
$P_3N_3ClF_5$	0.91 ± 0.02
$P_3N_3Cl_2F_4$	0.96 ± 0.08

b. Toxicity. Except for those compounds containing phosphorus-halogen bonds, the phosphonitriles appear to have very low toxicities.

c. Materials Compatibility. The phosphonitriles are expected to have very good materials compatibilities, due to some extent to their high molecular weights.

d. Colligative Properties. The simple halogenated phosphonitriles (*e.g.*, $P_3N_3X_6$) are low volatility materials. The alkoxy phosphonitriles have even higher boiling points; one of the simplest, $P_3N_3(OCH_2CF_3)_6$, has a boiling point of 70 °C at 0.02 kPa. Blending with, *e.g.*, hydrofluoroethers (HFEs) may give better distribution properties.¹⁰⁴

e. Atmospheric Impact. As with the phosphorus acids and esters, it is unlikely that phosphonitriles would have any global environmental impact. This is particularly true due to their very low volatilities.

f. Overall Assessment. A number of phosphonitriles have been shown to be excellent extinguishants in laboratory and carefully controlled field conditions; however, the exceedingly low volatilities make it unlikely that these could be practical total flooding extinguishants unless delivered as mists. To the extent misting is practical for suppressing aircraft fires, this family is worth a further look.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied		X	
Completely unstudied			
Estimated			

C. Phosphorus Halides

a. Fire Suppression Effectiveness. The following table shows the high effectiveness of compounds containing direct phosphorus to halogen bonds in reducing the burning velocities of hexane flames relative to halon 1301 (CF_3Br).¹⁰⁹ Multiple values for a particular compound are from different investigators as reported in the survey paper cited. Note that these results are true for low concentrations, where chemistry is believed to play a major role. At higher concentrations, the effects of heat capacity and dilution may make the relative efficiencies smaller. POCl_3 is about 10 times more effective than an equivalent amount of chlorine.¹¹² Of particular interest is that there appears to be little difference between the chlorine-containing and the bromine-containing compounds. This may indicate that phosphorus plays a primary role. Flame inhibition results do not always translate to flame suppression efficiency. There is one report¹¹³ of PBr_3 effectiveness on real-scale flames, indicating an effectiveness two orders of magnitude better than halon 1301.

Compound	Efficiency Relative to Halon 1301
PCl_3	6.7, 6.9
PBr_3	4.6, 6.9
O=PCl_3	5.2
S=PCl_3	8
S=PBr_3	6.7, 6.9

b. Toxicity. Compounds containing direct phosphorus to halogen bonds hydrolyze readily, forming injurious phosphorus-containing acids and halogen halides. For example, phosphorus tribromide will hydrolyze to give H_3PO_3 and HBr . Although there is some indication that hydrolysis is likely to be lower for fluorine-phosphorus bonds than for bonds of phosphorus with other halogens, hexafluorocyclotriphosphazene ($\text{P}_3\text{N}_3\text{F}_6$) has been shown to be toxic in a manner consistent with hydrolytic formation of acids.¹¹⁴ Further study is needed to determine whether perfluorinated compounds will have a sufficiently low hydrolysis rate to give them an acceptable toxicity.

c. Materials Compatibility. Owing to ready acid formation from hydrolysis, compounds of phosphorus containing phosphorus-halogen bonds are expected to be highly corrosive toward metals. Materials compatibility may be less of a problem for such compounds as PF_3 and O=PF_3 , where the rate of hydrolysis may be lower.

d. Colligative Properties. The adjacent table contains data for several phosphorus halides^{15,18}. As expected, volatility decreases with decreasing fluorine content and increasing bromine content. In some cases (*e.g.*, PCl_3 and PBr_3), there are surprisingly large liquid ranges.

Compound	MP (°C)	BP (°C)	ΔH_v (kJ/mol)
PF_3	-151.5	-101.5	16.5
PF_2Br		-16	23.9
PCl_3	-112	76	30.5
PBr_3	-40	173	38.8
O=PF_3	-39.1 ^a	-39.7 ^b	22.1
$\text{O=PF}_2\text{Br}$		32	29.7
O=PCl_3	1	105.5	34.4

^a Triple point.

^b Sublimation point.

e. Atmospheric Impact. These compounds should hydrolyze rapidly, giving products that would rain out.

f. Overall Assessment. There are some enticing flame data on phosphorus halides. Thus, despite the expected or known high toxicities and corrosiveness, it would be valuable to verify the flame suppression data. Further, it would be useful to examine the possibly more stable, totally fluorinated compounds, PF_3 and $\text{O}=\text{PF}_3$.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied		X	
Completely unstudied			
Estimated			

D. Phosphines

Phosphines have the general formula $PR_1R_2R_3$, where the substituents are alkyl, aryl, and/or hydrogen.

a. Fire Suppression Effectiveness. No flame suppression information is available on alkylphosphines, although the condensed phase chemicals are good flame retardants. Nonfluorinated phosphines are flammable, and it is not clear that fluorination will decrease this. For example, $P(CF_3)_3$ is reported to be spontaneously flammable.¹¹⁵

b. Toxicity. PH_3 is highly toxic. Few quantitative data exist on the toxicity of substituted phosphines.

c. Materials Compatibility. Phosphines can react with metals.

d. Colligative Properties. Phosphines will generally be more volatile than many of the other phosphorus compounds discussed here. This is due to their lower molecular weights and polarities.

e. Atmospheric Impact. Though one can propose reactions such as $PO + O_3 \rightarrow PO_2 + O_2$ coupled with $PO_2 + O \rightarrow PO + O_2$ that could deplete ozone, there is no evidence that such reactions would be effective in ozone depletion. There are no data on partially fluorinated phosphines.

f. Overall Assessment. Even with the expected higher volatilities, toxicity and flammability considerations indicate that phosphines are unlikely candidate fire suppressants.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied			
Completely unstudied	X		
Estimated			

E. Pentacoordinate Phosphorus

a. Fire Suppression Effectiveness. Compounds containing bromine are expected to be good suppressants though probably no better than corresponding trivalent compounds.

b. Toxicity. Only compounds where most or all of the groups are halogen atoms are stable. This is due to two factors. First, direct substitution stabilizes the higher oxidation state (+5). Second, there is decreased steric bulk from halogen atoms than from organic substituents. Halogen atoms attached to phosphorus are, however, subject to hydrolysis, leading to significant toxic hazard.

c. Materials Compatibility. Owing to ready acid formation upon hydrolysis, compounds of phosphorus containing phosphorus to halogen bonds are expected to be highly corrosive toward metals except, possibly, in totally anhydrous conditions..

d. Colligative Properties. In general, due to their higher molecular weight (five groups attached to the central atom), the pentacoordinate compounds have relatively low volatilities.

e. Atmospheric Impact. The pentacoordinate phosphorus compounds, all of which contain halogen directly bonded to the phosphorus, are expected to have very short atmospheric lifetimes due to hydrolysis and rainout and, therefore, low or zero GWP and ODP values.

f. Overall Assessment. The expected high toxicities, low stabilities, and poor materials compatibilities make these compounds unattractive for study.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied			
Completely unstudied	X		
Estimated			

VI. Metal-containing Compounds

A. Alkali Metal Compounds

Alkali metal compounds containing Na, K or Rb bound to inorganic or organic ligands are almost always ionic solids. Consequently, their use is limited to applications where powdered fire suppressants and solutions are effective.

a. Fire-Suppression Effectiveness. The inhibition effectiveness of compounds containing alkali metals is high. The approximate relative effectiveness of the potassium compounds K_2SO_4 and $KHCO_3$ relative to CF_3Br is 14 to 17 based on flame measurements in a methane flame.¹¹⁶ The literature contains numerous data on suppression concentrations of these compounds. Unfortunately, there is considerable scatter in these data. The results appear to depend on the size of the particles and the delivery procedure. Reported values for the suppression volume fractions (cup burner, *n*-heptane) of $NaHCO_3$ and $KHCO_3$ were 1.06 %¹¹⁷ and 0.78 %¹¹⁸, respectively. The relative order of suppression effectiveness of alkali metal compounds is $Rb > K > Na$.^{119,120}

Fire suppression studies have been conducted on the following compounds: K_3AlF_6 , $KF \cdot 2H_2O$, KI, KCl, KBF_4 , KBr, KF, Na_3AlF_6 , Na_2SiF_6 , NaCl, NaBr, NaBr in $CaCl_2$, NaF, NaI, K_2CrO_4 , K_2SO_4 , Na_2SO_3 , $Na_2S_2O_2 \cdot 5H_2O$, K lactate (water solution), K acetate (water solution), NaAcAc, $Na_2C_4H_4O_6 \cdot 2H_2O$, $KHO_3 \cdot urea$, $KHCO_3$, K, K_2CrO_4 , K_2CO_3 , K_2CO_2 , $K_2C_2O_4$, $K_4Fe(CN)_6 \cdot 3H_2O$, KOH, KNO_3 , Na_2CrO_4 , $NaHCO_3$, Na, $NaNO_3$, NaOH, $NaC_2H_3O_2 \cdot 3H_2O$, Na_2CO_3 , $Na_2C_2O_4$, $Na_2[Fe(CN)_5NO] \cdot 2H_2O$, $Na_4Fe(CN)_6 \cdot 10H_2O$, $Na_2B_4O_7 \cdot 10H_2O$, RbCl, RbBr, RbI.

b. Toxicity. The toxicities of the alkali metal cations range from very low to moderate. Sodium and potassium cations are normal physiological constituents and should therefore have minimal toxicity. Lithium salts are administered to humans suffering from bipolar personality abnormalities and are known to have toxic effects at doses exceeding about 2 g.¹²¹

c. Materials Compatibility. Alkali metal compounds can be very corrosive.

d. Colligative Properties of Some Compounds

Compound	BP (°C)	MP (°C)
$KHCO_3$	Decomposes	
KI	1420	723
K_2SO_4		1072
Na_2CO_3	Decomposes	851
$Na_2B_4O_7 \cdot 10H_2O$ (borax)	1575	741
NaI	1300	651

e. Environmental Impact. Since alkali metal compounds are generally water soluble, they will rain out readily and their atmospheric impact would be small. The impact of the alkali metal cations on ground systems is minimal. Any concerns would be due to the accompanying anionic components.¹¹⁴

f. Overall Assessment . The fire suppression effectiveness of these compounds has already been established. The only research issue is how to effectively deliver them to the fire, which is being addressed in other NGP projects.

	No Further Study	Further Study	High Priority for Further Study
Well studied	X		
Lightly studied			
Completely unstudied			
Estimated			

B. Compounds of Alkaline Earths

Inorganic compounds of alkaline earths containing Mg, Ca, or Ba, are almost exclusively solids. Consequently, their use is limited to applications where dry chemical fire suppressants and solutions are effective.

a. Fire-Suppression Effectiveness. Calcium- and magnesium- containing compounds were found to be ineffective fire suppressants additives (CaCO_3 , Ca(OH)_2 , Ca_2F_6 , $\text{CaSO}_4 \cdot \text{H}_2\text{O}$, MgCO_3 , $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$, MgCl_2).^{122,116, 123,124} Fire suppression properties of barium compounds are questionable. BaSO_4 was found ineffective for suppression of a methane flame.¹²² Ewing *et al.*¹¹⁸ found that the suppression volume fraction of BaSO_4 is 1.5 % for an *n*-heptane flame. Bulewicz and Padley¹²⁵ [6] found significant radical recombination rates for $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, BaSO_4 , $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$, and $\text{Ba(NO}_3)_2$.

b. Toxicity. Toxicities of compounds containing the alkaline earth cations (Mg, Ca) are generally low. Magnesium and calcium are both required for physiologic functioning and are believed to cause no systematic poisoning.¹²¹ However, some MG salts (*e.g.*, $\text{Mg}_3(\text{AsO}_3)_2$, MgCrO_4 , Mg(CN)_2) are known to be toxic. The soluble barium salts are poisonous when taken orally. The usual result of exposure to barium sulfide, barium oxide, and barium carbonate is irritation of the eyes, nose, mouth, and skin.

c. Materials Compatibility. These compounds should be compatible with most materials.

d. Colligative Properties

Compound	BP (°C)	MP (°C)
BaSO_4		1600, decomposes
$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$		113 (the apparent MP caused by loss of crystal water)
CaCl_2	1935	772
$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	1450	
CaCO_3		825, decomposes
Ca(OH)_2		580, decomposes
MgSO_4		200, decomposes
MgCl_2	1412	708

e. Environmental Impact. The environmental impact of alkaline earth compounds (Mg, Ca) is expected to be minimal.¹¹⁴

f. Overall Assessment. There is no evidence that these compounds are effective suppressants.

	No Further Study	Further Study	High Priority for Further Study
Well studied	X (Ca)		
Lightly studied	X (Ba,Mg)		
Completely unstudied			
Estimated			

C. Boron and Aluminum Compounds (Group III Elements)

Inorganic and organic compounds of boron and aluminum generally have very low vapor pressures and are, therefore, only suitable for applications where suppression by dry chemicals or solution is effective.

a. Fire-Suppression Effectiveness. There is little evidence of fire suppression capabilities of B- and Al-containing compounds. They were found to be ineffective in suppression of hydrocarbon flames.^{114,126,116,124,127} Inhibition effectiveness of some compounds is due to the presence of other effective elements in the molecule. The list of studied compounds includes: K_3AlF_6 , Na_3AlF_6 , Al_2Cl_6 , Al_2O_3 , $Al_2(SO_4)_2 \cdot 12H_2O$, BCl_3 , BF_3 , $B(OCH_3)_3$, KBF_4 , BBr_3 , $Na_2B_4O_7 \cdot 10H_2O$

b. Toxicity. Although borates and boric acid are widely used, boron-containing compounds are moderately toxic. The fatal oral dose of boric acid for an adult is approximately 15 g to 20 g.¹¹⁴ Some aluminum compounds are irritants or toxic owing to the presence of the other constituents. Normally, aluminum compounds are of low toxicity.

c. Materials Compatibility. Aluminum bromide and aluminum chloride exhibit corroding effects.

d. Colligative Properties

Compound	BP (°C)	MP (°C)	ΔH_v (kJ/mol at BP)
$AlCl_3$	183	190 (253 kPa)	
$Al_2(SO_4)_3$		770, decomposes	
$AlCl_3$	183 (100 kPa)	190 (252 kPa)	
BF_3	-99.9	-126.8	
$B(OCH_3)_3$	68	-29	37

e. Environmental Impact. Boron and aluminum compounds do not exhibit environmental impact since they are a common component of many soils and minerals.

f. Overall Assessment. There is no evidence that these compounds are effective suppressants.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied	X		
Completely unstudied			
Estimated			

D. Copper-containing Compounds

This includes inorganic and organic compounds containing divalent or monovalent Cu.

a. Fire-Suppression Effectiveness. The existing data on the fire suppression efficiency of these compounds is contradictory. CuO was found to be ineffective for suppression of a methane flame¹²⁸ and was characterized as a thermal inhibitor.¹²⁴ Cuprous chloride (CuCl), however, was found to be an effective inhibitor in methane flames. The inhibition effectiveness of CuCl relative to CF₃Br is 4 to 12 based on flame speed measurements in methane/air flames.¹¹⁶ Dolan and Dempster¹²⁸ found that copper acetate monohydrate, copper carbonate, Cu₂O, CuO, CuCl, and CuCl₂ were all ineffective at suppressing the ignition of methane/air flames.

b. Toxicity. Copper is one of several metals that are essential to life. Copper metal is non-toxic. The inhalation of dusts, fumes, and mists of copper salts, however, can cause congestion of the nasal and mucous membranes, occasionally producing perforation of the nasal septum. Toxicity (oral) of Cu₂O is high: the LD₅₀(rat) is 470 mg/kg.¹²⁹ The LD₅₀(oral, human) for CuCl is 200 mg/kg. Copper chloride and sulfate have been reported as causing irritation of the skin. Cuprous oxide is irritant to the eyes and upper respiratory tract.

c. Materials Compatibility. There are no known issues.

d. Colligative Properties. The inorganic salts are all solids and would need to be used as a dispersed aerosol. As shown in the following table, the boiling points of the organometallic compounds could be considerably lower. Whether fluorination would bring any of them into a useful range for dispersion as a neat fluid remains to be seen.

Compound	BP (°C)	MP (°C)
CuO	1026, decomposes	
Cu ₂ O	1800, decomposes	1235
Cu(C ₂ H ₃ O ₂) ₂ ·H ₂ O	214	200
CuCl ₂		498
CuCl	1366	422

e. Environmental Impact. Copper is both an essential and potentially toxic element.¹²¹ There are health related effects associated with either too little or too much in the environment. There are concerns that copper plays a role in the catalytic formation of chlorinated dioxins during incineration. Agricultural soils with a limit of 2 kg to 3 kg Cu per year are considered acceptable. In Switzerland, the limit for drinking water is 1.5 mg/kg Cu.

f. Overall Assessment. The fire suppression effectiveness of copper-containing compounds is still open to question. A short set of screening tests would indicate whether further examination is warranted.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied		X	
Completely unstudied			
Estimated			

E. Titanium-containing Compounds

These include compounds containing tetravalent Ti bound to inorganic or organic ligands. The +1 and +3 oxidation states exist, but have not been studied.

a. Fire-Suppression Effectiveness. Only one titanium-containing compound (TiCl_4) has been investigated, and its fire suppression efficiency is high. The coefficient of effectiveness of TiCl_4 relative to CF_3Br is 5.5 based on flame speed measurements in hydrogen/air and hexane/air flames.^{106,126} Data on suppression concentrations are absent. Other common titanium compounds are high-melting solids, which make them unsuitable for use as fire suppressants.

b. Toxicity. Titanium metal is non-toxic. Thus, the harmful effects of some of these compounds derive from products of the anion (*e.g.*, hydrochloric acid in the case of titanium tetrachloride). Titanium is not absorbed or accumulated in the human body. The toxicity of TiCl_4 is high (inhalation): the LC_{50} (mice) is 10 mg/m^3 for 2 hrs.

c. Materials Compatibility. TiCl_4 is highly reactive and corrosive. It liberates HCl on contact with H_2O .

d. Colligative Properties

Compound	BP (°C)	MP (°C)	ΔH_v (kJ/mol at BP)
TiCl_4	136	-30	39

e. Environmental Impact. It was suggested that titanium should not be considered within the scope of human monitoring. Titanium dioxide is classified as a nuisance dust.¹²¹ Monitoring may be necessary in the case of other titanium compounds as organic titanium derivatives.

f. Overall Assessment. While TiCl_4 is an effective suppressant and does have some volatility, it is not suitable for routine use as an extinguishant because of its tendency to liberate HCl. Other common Ti compounds, such as TiO_2 , are solids and do not appear to have properties that would make them more attractive candidates than other metallic compounds recommended in this report.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied	X		
Completely unstudied			
Estimated			

F. Manganese-containing Compounds

These are compounds containing Mn bound to inorganic or organic ligands. Manganese occurs naturally in ionic salts as Mn^{+2} . Synthetic compounds, however, are known in nearly all valences between -3 and $+7$.

a. Fire-Suppression Effectiveness. There are practically no data on fire suppression properties of manganese-containing compounds. Manganese acetylacetonate is a very effective inhibitor based on data obtained from an ethanol/air counterflow burner experiments. It was found to be more effective than iron pentacarbonyl on a molar basis.¹¹⁹ Methylcyclopentadienyl manganese tricarbonyl (MMT) is well known as an antiknock fuel additive.

b. Toxicity. Although inorganic manganese compounds tend to be low in toxicity, the more volatile organometallics (those containing metal to carbon bonds) are likely to be more toxic. Fumes and dust of manganese compounds can cause central nervous system and pulmonary system damage. Chronic poisoning is possible for exposures over several months. LC_{50} (rat, inhalation, 7 hr) for MMT is 76 mg/m^3 and LD_{50} (rat, oral) is 50 mg/kg .¹²⁹

c. Materials Compatibility. There are no known issues.

d. Colligative Properties.

Compound	BP (°C)	MP (°C)
MMT	106 (1.6 kPa)	-0.75
$MnBr_2$	1027	698
MnI_2	1017	613

e. Environmental Impact. Manganese compounds do not present any known environmental risks.¹²¹ There are some regulations on the maximum allowable levels. The maximum allowable concentration at workplaces for an 8 hour day is up to 5 mg/m^3 in the U.S.¹²¹

f. Overall Assessment. There is a paucity of data on the fire suppression properties of these compounds, but what little there is points to a high degree of effectiveness.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied			X
Completely unstudied			
Estimated			

G. Antimony-containing Compounds

Antimony may exist in oxidation states -3 , $+3$, $+4$ or $+5$. More than 3000 organic antimony compounds are known.

a. Fire-Suppression Effectiveness. The fire suppression efficiencies of antimony containing compounds are high. The coefficient of effectiveness of SbCl_3 relative to CF_3Br is 4.6 based on flame speed measurements in hydrogen/air and hexane/air flames.^{130,126} Data on extinction concentrations of antimony compounds are absent. Fire suppression data are available for the following antimony compounds: SbCl_3 , SbCl_5 , and SbBr_3 . The corresponding iodides (SbI_3 and SbI_5) are also stable, but have not been tested for fire suppression effectiveness.

b. Toxicity. Most antimony-containing compounds are highly toxic via oral, inhalation and intraperitoneal routes. Locally, these compounds are irritant to the skin and mucous membranes. Toxicity (inhalation) of SbCl_3 is very high; the $\text{TC}_{\text{LO}}(\text{human})$ is 73 mg/kg.¹²⁹

c. Materials Compatibility. Antimony trichloride is highly reactive and corrosive. It liberates HCl upon contact with H_2O .

d. Colligative Properties.

Compound	BP (°C)	MP (°C)
SbCl_3	283	73
SbCl_5	3	79
SbBr_3	280	96.6

e. Environmental Impact. Some antimony compounds (*e.g.*, Sb_2O_3) are known to be carcinogenic. There are industrial standards limiting worker exposure to particulates.¹²¹ Zoller¹³¹ cites evidence for the introduction of Sb into the environment through incineration and dumping. There are industrial standards for limiting workplace exposure to Sb particulates, which range from 0.2 mg/m^3 to 2 mg/m^3 .

f. Overall Assessment. The potential as fire suppressants is offset by concerns about the high toxicity and environmental impact of these compounds.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied	X		
Completely unstudied			
Estimated			

H. Germanium-containing Compounds

These are compounds containing divalent or tetravalent Ge bound to inorganic or organic ligands.

a. Fire Suppression Effectiveness. Although data on the interaction of germanium-containing compounds with flames is limited, there is some indication that some of these compounds may possess a high degree of fire suppression efficiency. The coefficient of effectiveness of GeCl_4 relative to CF_3Br is 2.2 based on flame speed measurements in hexane/air flames.¹⁰⁶ It is not clear whether the observed inhibition is due to the Ge itself or the ability of the GeCl_4 to deliver Cl atoms into the reaction zone of the flame.

b. Toxicity. Germanium compounds are considered to be of low toxicity. Little is known about the toxicity of organic germanium compounds; they may resemble other organometallics in having higher toxicity than inorganic forms. The toxicity of GeCl_4 is moderate (irritation to skin, eyes).¹²⁹

c. Materials Compatibility. Liberates toxic fumes of chlorides when heated or upon reaction with H_2O [2].

d. Colligative Properties.

Compound	BP (°C)	MP (°C)	ΔH_v (kJ/mol at BP)
GeF_2	130	110	
GeF_4	-36.5		
GeCl_4	83	-49.5	35
GeBr_2	150	143	
GeBr_4	186	26	

e. Environmental Impact. Unknown. There are no air or occupational standards for germanium, except germanes in the USA. The ecotoxicity of these compounds is also considered to be low.¹²¹

f. Overall Assessment. Although there is evidence that indicates the germanium halides are effective suppressants, this potential is offset by cost and materials compatibility issues.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied	X		
Completely unstudied			
Estimated			

I. Silicon-containing Compounds

These compounds contain tetravalent Si bound to inorganic or organic ligands.

a. Fire-Suppression Effectiveness. Data on flame suppression demonstrate ineffectiveness of silicon containing compounds.^{124,128} Burning velocity measurements of inhibited n-hexane flame (SiCl_4 , $\text{Si}(\text{CH}_3)_4$) indicate that silicon compounds may have some inhibition effectiveness at low concentration additions.¹⁰⁶ List of studied compounds: SiCl_4 , SiHCl_3 , SiF_4 , Na_2SiF_6 , SiO_2 , $\text{Si}(\text{CH}_3)_4$.

b. Toxicity. Compounds containing silicon directly bonded to halogens are highly toxic owing to rapid hydrolysis of the silicon-halogen bond. Limited testing of industrial chemicals indicates that stable silane derivatives have a low toxicity.¹²⁹ A number of siloxanes used industrially have a low toxicity. Toxicity of SiCl_4 is moderate via inhalation route.¹²⁹

c. Materials Compatibility. The silicon halides, including SiF_4 and SiCl_4 , liberate acid gases (HF and HCl) upon reaction with H_2O .

d. Colligative Properties.

Compound	BP (°C)	MP (°C)	ΔH_v (kJ/mol at BP)
SiF_4	-65	-77	22
SiCl_4	58	-70	32
$\text{Si}(\text{CH}_3)_4$	27		27

e. Environmental Impact. Silicon is a common element and significant terrestrial environmental impacts due only to silicon itself are unlikely. There are industrial standards limiting worker exposure to particulates. Estimations reported indicate that silicon compounds containing bromocarbon substituents should have atmospheric lifetimes on the order of days and ODP values less than 0.02.¹¹⁴

f. Overall Assessment. Compounds containing a silicon-halogen bond are unacceptable due to their tendency to liberate HCl (or other acid gases) upon reaction with H_2O ; organosilicon compounds, such as TMS, are flammable. There do not appear to be any other members of this family of compounds having properties that would make them superior candidates to the other compounds recommended in this report.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied	X		
Completely unstudied			
Estimated			

J. Iron-containing Compounds

These compounds contain Fe bound to inorganic or organic ligands.

a. Fire Suppression Effectiveness. The fire suppression efficiency of iron-containing compounds is high. The coefficient of effectiveness of iron pentacarbonyl and ferrocene relative to CF_3Br is 50-100 based on flame speed measurements in methane/air and hexane/air flames.^{106,132,133} Measured extinction concentrations for iron pentacarbonyl are 1.7 % (ethanol flame¹³⁴) and 0.23 % for methane flame (0.01atm).¹³⁵ Ewing et al., found 0.08 % to 0.1 % for $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ in an n-heptane flame.¹¹⁸ The list of iron containing compounds for which flame suppression and/or extinction data exists include: iron pentacarbonyl, ferrocene, iron acetylacetonate, $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, $\text{K}_4\text{Fe}(\text{CN})_6$, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$, $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$, $\text{Fe}(\text{CF}_3\text{-CO-CH=CO-CF}_3)_3$

b. Toxicity. A number of iron compounds have relatively low toxicity. Highly volatile iron compounds are more likely to be toxic. Iron pentacarbonyl is highly toxic, a lung irritant, and causes damage to kidneys and liver.¹¹⁴ The toxicity of ferrocene, however, is considered to be moderate (oral): $\text{LD}_{50}(\text{rat}) = 1350 \text{ mg/kg}$.¹²⁹

c. Materials Compatibility. We are not aware of any properties of these compounds that make them incompatible with materials used in the construction of the weapons platform or storage/dispersion device.

d. Colligative Properties.

Compound	BP (°C)	MP (°C)	ΔH_v (kJ/mol at BP)
Ferrocene		174 (sublimes)	
$\text{Fe}(\text{CO})_5$	103	-25	38
Iron acetylacetonate		69 (sublimes)	

e. Environmental Impact. Not regulated. None of the transition metal compounds are expected to show global environmental impact due to the metal itself.

f. Overall Assessment. The high flame inhibition effectiveness of these compounds has already been established, but no flames or fires have been suppressed by an iron-containing compound. There is also the issue of their effective delivery to the fire, which is being addressed in other NGP projects.

	No Further Study	Further Study	High Priority for Further Study
Well studied		X	
Lightly studied			
Completely unstudied			
Estimated			

K. Tin Compounds

These compounds contain either divalent or tetravalent Sn bound to inorganic or organic ligands.

a. Fire Suppression Effectiveness. The fire suppression efficiency of tin-containing compounds is expected to be high. The coefficient of effectiveness of SnCl_4 relative to CF_3Br is 5.7 based on flame speed measurements in hydrogen/air and hexane/air flames.^{106,126} The fire suppression efficiencies of the following tin containing compounds have been investigated: SnCl_2 , SnCl_4 , $\text{Sn}(\text{CH}_3)_4$

b. Toxicity. The biological effects of tin compounds are almost exclusively determined by the nature and the number of groups bound to the tin atom.¹²¹ Inorganic tin salts are of low order of toxicity. Tin halides, including SnCl_2 and SnCl_4 , are known to undergo rapid hydrolysis forming acid halides, which are toxic by inhalation.¹²⁹ Some organotin compounds exhibit acute toxicity that generally decreases in the order $\text{R}_3\text{SnX} > \text{R}_2\text{SnX}_2 > \text{RSnX}_3$, where R is a covalently bound organic ligand and X represents an anionic group attached to the tin via an electronegative atom such as a halogen or oxygen.¹²¹

c. Materials Compatibility. The tin halides are highly reactive and corrosive due to the formation of HCl and/or other acids upon contact with H_2O .¹²⁹

d. Colligative Properties.

Compound	BP (°C)	MP (°C)	ΔH_v (kJ/mol at BP)
SnCl_2		37	
SnCl_4	114	-33	37
$\text{Sn}(\text{CH}_3)_4$	78	-35	
$\text{Sn}(\text{CH}_3\text{CH}_2)_4$		-131	

e. Environmental Impact. The environmental impact of water soluble, inorganic tin compounds is minimal. However, the aquatic toxicity of certain trialkyl and triaryl tin compounds is a concern. Tributyltin and triphenyltin, which are the active ingredients in antifouling paints for ships, appear to be highly toxic towards aquatic life.¹²¹

f. Overall Assessment. The existing data suggests a degree of high fire suppression efficiency and low environmental impact for these compounds.

	No Further Study	Further Study	High Priority for Further Study
Well studied			
Lightly studied			X
Completely unstudied			
Estimated			

VII. CONCLUSION

As part of the search for fire fighting technologies alternative to halon 1301, the authors have reviewed the available data on the universe of chemical families. The search focused on fire-suppression effectiveness, toxicity, materials compatibility, colligative properties, and environmental impact. For each family, there is an evaluation of worthiness of further examination. The following table summarizes those families for which future examination was deemed valuable.

Chemical Family	Recommendation		
	High Priority	Further Study	Quick Look
Iodine-containing alkanes		X	
Iodine-containing 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		
Bromofluorosulfides			
Sulfoxides			X
Phosphorus-containing Acids and Esters	X		X
Phosphonitriles		X	
Phosphorus halides		X	
Copper-containing Compounds			X
Manganese-containing Compounds	X		
Iron-containing compounds		X	
Tin-containing compounds	X		

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