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Construction of an Exploratory List of Chemicals to Initiate the Search for Halon Alternatives

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EXECUTIVE SUMMARY

The objective of this project is to initiate a systematic search for optimal halon replacements by identifying approximately 100 gases and/or liquids, covering a range of chemical and physical principles thought to affect flame suppression capability. This comprehensive report is designed to provide a basis for the search for alternatives to the current commercial halons. As much detail as possible is provided for each of the 103 chemicals to aid researchers who might test or evaluate these chemicals in the future.

The current commercial halons have been identified as contributing to the depletion of the earth's stratospheric ozone. As a result, their manufacture has been limited to 1986 levels by the Montreal protocol, and more severe limitations are anticipated in the near-future. This project is an early step in a government/industry program to identify and qualify candidate replacements for halons 1301 and 1211 that will satisfy the needs of the major users for existing applications. No such search has been conducted since the late 1940s, when the U.S. Army conducted the study that led to today's predominant halogenated fire suppressants: halons 1301 (CF_3Br) and 1211 (CF_2ClBr). Halon 2402 ($C_2F_4Br_2$) is in use to a lesser degree, as are halons 1001 and 1011.

Replacements for the current halons must have a number of critical properties: fire suppression efficiency, low residue level, low electrical conductivity, low metals corrosion, high materials compatibility, stability under long-term storage, low toxicity (inhalation and contact) of the chemical and its combustion products, and low (or zero) contributions to stratospheric ozone depletion and global warming. These constraints are expected to complicate the search.

The search strategy selected by the National Institute of Standards and Technology (NIST) team focusses on principles for efficient fire suppression and low contribution to stratospheric ozone depletion. The widest range of chemical families were researched for their potential to test these principles. Some of these families have not previously been considered for fire suppression. Compounds are discussed which are clearly not candidates as alternatives, but which are included to test principles of fire suppression or ozone depletion.

As a basis for deriving these principles, this report begins with a compilation of state-of-the-art knowledge in flame suppression and ozone depletion chemistry. The means by which a chemical can quench a flame fall under the following headings:

- Physical mechanisms
  - smothering or blanketing
  - cooling and dilution
  - mechanical means (e.g., blowing out a match)
  - flame radiation blockage
- Chemical action (interference with the chain reactions that propagate flames)

All agents have physical effects on a fire. Agents which also have a chemical mechanism, such as the currently-used halons, are more effective due to the additional pathway for flame suppression. There have been several studies of the effectiveness of specific chemicals. Very few of those separate the contribution of physical and chemical mechanisms.

The means for altering a chemical to decrease its contribution to ozone depletion also fall under a few headings:

- Elimination of all bromine, chlorine, and iodine atoms;
- Increased reactivity in the lower atmosphere by
  - enhanced reaction with OH radicals
  - dissociation due to absorption of solar radiation
  - enhanced rain out due to increased polarity

Assessment of ozone-depletion effectiveness is based on atmospheric modeling. The only experimental work is the determination of possible reaction paths and their rates.

An extensive search was performed of the literature on combustion suppression, flame inhibition, and fire retardancy. This led to the identification of nine families of chemicals with potential for workbench testing of the above principles.

- Saturated halocarbons or halons: ($C_nF_oCl_pBr_qI_r$ where $o+p+q+r=2n+2$). These are analogs of the currently-used halons and include totally fluorinated compounds, photosensitive compounds, and analogs to the HCFCs.
- Halogenated ketones, anhydrides, and esters. These contain C=O bonding and may be more prone to solar dissociation in the troposphere.
- Unsaturated halocarbons. These contain C=C bonding and may be more reactive with OH in the troposphere.
- Halogenated ethers. These contain an O-C-O linkage, which is thought to promote solar dissociation in the troposphere.
- Halons containing iodine. These are likely to be more reactive in the troposphere.
- Sulfur halides. These are analogs to the halons.
- Compounds containing phosphorus. These are non-ozone-depleting, possibly highly efficient fire suppressants.
- Silicon and germanium compounds. These are tropospherically-reactive analogs to the halons.
- Metallic compounds. These are extremely efficient fire inhibitors that are non-ozone-depleting.
- Inert gases. These are baseline chemicals: less-efficient, only physically active agents with zero ozone-depletion potential.

While it is true that some of the chemicals which appear on this list can be considered candidates themselves, others were chosen to test principles of fire suppression. The appendix contains data sheets for

A list of 103 chemicals which were selected from these families follows:

perfluoromethane
perfluoroethane
perfluoropropane
perfluoro-n-butane
perfluorocyclobutane
trifluoromethane
pentafluoroethane
1,1,1,2-tetrafluoroethane
dibromodifluoromethane
2,2-dibromo-1,1,1,2-tetrafluoroethane
chlorodifluoromethane
1,1,1-trichlorethane
2,2-dichloro-1,1,1-trifluoroethane
2-chloro-1,1,1,2-tetrafluoroethane
1,1-dichloro-1-fluoroethane
1-chloro-1,1-difluoroethane
bromodifluoromethane
bromochlorofluoromethane
2-bromo-2-chloro-1,1,1-trifluoroethane
2-bromo-1-chloro-1,2,2-trifluoroethane
1-bromo-1,1,2,2-tetrafluoroethane
2-bromo-1,1,1-trifluoroethane
1,2-dibromo-1,1,2-trifluoroethane
1,2-dibromo-1,1-difluoroethane
1,2-dibromo-1,2-difluoroethane
1-bromo-1,1,2,3,3,3-hexafluoropropane
1,3-dibromo-1,1,3,3-tetrafluoropropane
2,2-dibromo-1,1,3,3-tetrafluoropropane
1-bromo-1,1,3,3,3-pentafluoropropane
hexafluoracetone
trifluoroacetic anhydride
bis(perfluoroisopropyl) ketone
methyltrifluoroacetate
3-bromo-1,1,1-trifluoropropanone
bromopentafluoroacetone
bromomethyltrifluoroacetate
perfluoropropene
perfluorobutene-2
perfluorotoluene
1,1,3,3,3-pentafluoropropene-1
3,3,3 trifluoropropene
1,2-bis(perfluoro-n-butyl)ethylene
3-bromoperfluoropropene
1-bromoperfluoropropene
1,2-bis(perfluoromethyl)ethylene
1-bromoperfluoromethyl-2-perfluoromethylethylene
1-bromo-bis(perfluoromethyl)ethylene
tetris(perfluoromethyl)ethylene
tetrafluorodimethyl ether
pentafluorodimethyl ether
2-chloro-1-(difluoromethoxy)-1,1,2-trifluoroethane
isoflurane
perfluoro-2-butyltetrahydrofuran
bis(bromodifluoroethyl) ether
1-bromo-1,1,3,3,3-pentafluorodimethyl ether
bromoenflurane
octafluorofuran
3-bromoperfluorofuran
bis(perfluoromethyl) thioether
tris(perfluoromethyl) amine
iodotrifluoromethane
chlorodifluoroiodomethane
1-bromo-1,1,2,2-tetrafluoro-2-iodoethane
1,1,2,2-tetrafluoro-1,2-diiodoethane
iodomethane
iodoethane
1-iodopropane
1,1,1,2,2,3,3-heptafluoro-3-iodopropane
sulfur fluoride
sulfur chloride fluoride
sulfur bromide fluoride
phosphorous trifluoride
phosphorous trichloride
phosphorous bromide difluoride
phosphoryl fluoride
phosphoryl chloride
phosphoryl bromide fluoride
tetrachlorosilane
trichlorofluorosilane
tetrafluorosilane
bromotrifluorosilane
tribromofluorosilane
tetramethylsilane
chlorotrimethylsilane
trichloromethylsilane
chloromethyltrimethylsilane
tetrachlorogermane
tetramethylgermane
sodium hydrogen carbonate
sodium acetate
potassium hydrogen carbonate
potassium oxalate
potassium acetate
potassium acetylacetonate
chromium acetylacetonate
chromyl chloride
tin (IV) chloride
titanium (IV) chloride
tetraethyl lead
iron pentacarbonyl
nitrogen
carbon dioxide
argon

each of the selected compounds that include formulae, common names, classification numbers, physical properties, commercial sources and prices (if available), toxicity information, references to fire suppression results, and additional relevant comments.

These compounds should be tested in a selective series of experiments based on the insights used in the development of the list. The study should determine the fire suppression effectiveness of these agents, and, if possible, characterize their mechanisms of chemical flame inhibition. Such insights will provide the knowledge base required for the intelligent design of alternative chemical fire suppressants with a full range of desirable properties.

The authors appreciate the sponsorship of this project by the Engineering and Services Laboratory, Air Force Engineering and Services Center, Capt. John M. Floden, Contract Monitor. The review provided by the Halon Alternatives Research Corporation, chaired by Ms. Denise Mauzerall, was extremely helpful. The final copy of this report was prepared and edited by Ms. Paula Garrett.

SECTION I

INTRODUCTION

A. OBJECTIVE

The objective of this project is to identify approximately 100 gases and/or liquids, covering a range of chemical and physical principles thought to affect flame suppression capability. This project is part of an overall effort to identify safe and effective fire suppression agents which are less detrimental to stratospheric ozone than the current commercial halons. A major element in the choice of compounds is also understanding the processes by which halons deplete stratospheric ozone. The list of compounds includes as much relevant information as possible to aid researchers who will use the findings of this work in the search for new flame suppressants.

B. BACKGROUND

1. Halogenated Hydrocarbon Fire Suppressants (halons)

a. Definition and Designation

Halogenated hydrocarbon fire suppressants refer to a group of chemical compounds widely used for firefighting and inerting (creation of an atmosphere which does not support combustion). The compounds denoted as halons contain one or more halogen atoms[1] attached to a backbone of one or more carbon atoms. Only straight chain, fully saturated (each carbon atom is bonded to four other atoms) compounds are included.

A simple nomenclature developed by the United States Army Corps of Engineers is widely employed to designate halons [1]. A particular halon is assigned a "halon number" where, reading from left to right, the first number is the number of carbon atoms and the remaining four numbers are the number of each halogen atom in order of increasing atomic weight, i.e., F, Cl, Br, and I. Any terminal zeros are dropped. As an example, trifluorobromomethane, CF_3Br, is denoted as halon 1301. Note that some inconsistencies are possible when two or more carbon atoms are present. Consider CBr_2HCBr_2H and CBr_3CBrH_2. Both of these molecules would be designated as halon 2004.

b. A Brief History

Ford [2] has provided a brief perspective on the historical development of halons for firefighting purposes. Carbon tetrachloride (halon 104) was the first halon to be used. Starting in the early 1900s and continuing until the mid-1960s, fire extinguishers containing this liquid were commercially available. In the late 1920s, methyl bromide (halon 1001) was found to be much more effective for fire-extinguishment. Because of its high toxicity, this compound was never widely utilized in the United States. It was employed

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[1] The five halogen atoms are: fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At). Astatine is very scarce and will not be considered further in this work.

militarily during World War II by the British (aircraft extinguishing systems) and Germans (aircraft extinguishing systems and marine systems) [1].

During World War II the Germans developed a fire-extinguishing agent known as "CB," chlorobromomethane (halon 1011), which was as effective as halon 1001 and less toxic. This agent was ordered to be installed on all German military aircraft, but apparently did not come into widespread use before the end of the war [1].

Following the war, the German research efforts were reviewed by the United States military; and, CB was extensively tested in this country [3]. CB was eventually adopted for use by the United States Air Force [4]. Despite the improvements represented by CB, it was recognized that significant toxicological problems remained and that fire suppression capabilities might be further refined. As a result, the Air Force [1] and the U.S. Army Corps of Engineers [5,6] began extensive testing of a wide range of possible compounds. These projects considered a number of possible firefighting agents, but the principal focus was the halons.

The requirements for a new agent specified by the agencies are instructive because they generally apply to so-called "clean" firefighting agents. Klein [1] lists the Air Force requirements as:

1. better extinguishing properties than CB over the temperature range of -54°C to 71°C,
2. less toxic than CB,
3. less corrosive than CB,
4. suitable for class A, B, and C fires[2], and
5. higher specific gravity than CB.

The Corps of Engineers' specifications [6] were similar. The agent was to be:

1. less toxic than carbon tetrachloride,
2. less corrosive than carbon tetrachloride,
3. a nonconductor of electricity,
4. stable when stored for five years in any climate, and
5. suitable for use over a temperature range of -54°C to 71°C.

These investigations identified four halons as being particularly promising [2]: trifluorobromomethane (halon 1301), bromochlorodifluoromethane (halon 1211), dibromodifluoromethane (halon 1202), and dibromotetrafluoroethane (halon 2402). Halons 1301 and 1211 have since been developed and are utilized for a large number of applications. Halons 1202 and 2402 are also used, but less extensively.

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[2] Fires are classified by the type of fuels and conditions present. Class A fires involve cellulosic materials such as wood or paper. Class B fires refer to liquid fuels such as hydrocarbons and alcohols. Fires where energized electronic components are present are denoted as Class C fires. If metal fuels such as sodium or aluminum are present, the fire is a Class D fire.

In this text these four halons will be denoted as "the current commercial halons" to differentiate them from the broader halon and halogenated organic molecular families. In the literature, the current commercial halons are often denoted simply as "halon."

Since the 1950s, the current commercial halons have come into widespread use for firefighting and fire protection systems. The military uses these compounds extensively in a number of mission-critical areas. Similarly, current commercial halon systems have been incorporated into a number of civilian uses where costly or irreplaceable facilities, equipment, or items must be protected from fire. By 1985, the production and use of these halons in the United States had reached 6.4×10^6 kg [7]. Halon systems are generally regarded as reliable, safe, and effective. As such, they have become an integral part of fire protection practice.

Unfortunately, a major issue has arisen which threatens to curtail, if not eliminate use of the current commercial halons. This issue has been discussed extensively in the literature. A chronological summary of major events in this area has been compiled by S. Daws [8]. Anderson [7] and Grant [9] provide excellent histories of the problem and prospects for future halon usage. A brief history is provided here to illustrate the nature of the problem and the suddenness with which it arose.

In 1974, Molina and Rowland [10] hypothesized that the release of chlorine by photolysis of manmade chlorofluorocarbons (CFCs) in the stratosphere would result in a reduction of the ozone concentration which shields the earth's surface from the sun's harmful ultraviolet radiation. By 1978, the use of CFCs as propellants for aerosols was banned in the United States for all but essential uses.

From 1978 to 1985, the movement of the global community toward the control of CFCs was very deliberate. This changed with the publication of results of ground-based observations indicating a 40 percent depletion of stratospheric ozone above the Antarctic at certain times of the year--the "ozone hole" [11]. Satellite observations confirmed this to be a regional effect [12]. World-wide decreases in stratospheric ozone have since been detected [13]. By 1988, there was sufficient evidence for most scientists to conclude that stratospheric ozone depletion has occurred as a result of ozone reactions with Cl and Br atoms introduced into the stratosphere by manmade CFCs and current commercial halons [13].

In September of 1987, the Montreal Protocol was signed by the United States, Canada, members of the European Economic Community, and 23 other countries. This accord set limits on the production of CFCs and halons 1211 and 1301 in an effort to limit further destruction of stratospheric ozone. Initial discussions had focused primarily on the CFCs, but in the final document, production of the two halons is limited to their 1986 levels. Note that the limits require a cut in manufacture because production has increased significantly since 1986. The protocol was effective as of January, 1989 and limits go into force in January, 1992.

Since the signing of the Montreal Protocol, evidence has continued to mount that halons contribute significantly to stratospheric ozone depletion. The current commercial halons are now recognized as being 3 to 11 times more destructive of stratospheric ozone on a molecule-per-molecule basis than the common CFCs due to the presence of bromine atoms in these fire suppressants [14]. It has been hypothesized that Br atoms can have even larger effects on ozone levels through a synergistic interaction with more abundant Cl atoms [15,16]. A recent study also suggests that atmospheric concentrations of halons 1211 and 1301 are increasing at annual rates of 12 percent and 5 percent, respectively [17]. These rates are much higher than previously believed.

These recent findings suggest that future accords may demand larger cuts in halon production than those mandated by the Montreal Protocol. During 1989, two bills were introduced in the United States Senate designed to limit the production of current commercial halons to levels lower than called for by the Montreal Protocol. The first mandates limiting production at 1986 levels as of July, 1989, with a

20 percent cut in 1992, a 50 percent cut in 1995, and a total ban in 1997. An exemption is provided for halon uses essential to national security needs. The second bill would place a surcharge on halons in 1992 of $1.50 per pound multiplied by the chemical's ozone depletion potential. For halon 1301 this would amount to approximately $15 per pound [9].

Future fire protection will, at a minimum, be considerably more expensive and more carefully controlled. It is also possible that all production of the current commercial halons will be halted and that the world will be dependent on supplies which have been stored or "banked" for fire protection requirements. Grant [9] refers to the current uncertainty concerning the future of halons as "one of the most challenging problems ever to confront the fire protection community."

c. Current Use of Halogenated Fire Suppression Agents

The current commercial halons are rapid and effective fire inerting agents and suppressants. They have low toxicity at ambient temperatures (note that the toxicity of combustion products resulting from the use of halons is treated as a separate issue to be discussed in Section I-C-3) so that they can be effectively used in the presence of people. In addition, these compounds: are available as both liquids and gases and can therefore be used either as streaming or flooding agents; they are clean, leaving little or no residue (with the possible exception of combustion products); they are nonconductive, so that they can be applied safely to energized electronic equipment; and they are compatible with a wide variety of plastics and metals.

The three most commonly used halons, 1301, 1211, and 2402, have physical properties which are compatible with two distinct modes of deployment. Halon 1301 is a gas at ambient temperatures and is most often used in "total flooding" applications. The gas is introduced into an enclosure or space at levels sufficient to suppress fires and prevent further ignition. Halon 2402 is a low-boiling-point liquid at normal room temperatures. As such, it is an ideal streaming agent for local application, which is its most common use. Halon 1211 has physical properties which are intermediate between 1301 and 2402 and has been used much the same as halon 2402.

The proceedings of a meeting held by the National Academy of Sciences cites many examples of where halons have been used [18]. The most important of these are facilities where "clean" agents are required and situations where personnel must remain during fire emergencies.

"Clean" fire extinguishing agents are often used when costly and/or irreplaceable objects are present. Libraries, museums, and archives of important national documents are examples of facilities which are currently protected by halon total-flooding extinguishment systems. Extinguishing agents such as water or dry powders would be very damaging in these environments. Clean agents are also required where other alternatives would interfere with important functions of a facility or device. Many computer facilities, electronic record depositories, and telephone exchanges are protected by current commercial halon total flooding systems. In this context, the lack of electrical conductivity is also crucial. Additional examples include the mission-critical use of these halons on Air Force flight lines to combat aircraft and hangar fires and their use to fight nacelle fires in both civilian and military jet engines.

There are also circumstances when the evacuation of personnel during a fire emergency is not feasible. Control rooms of nuclear reactors and aircraft carriers are examples of facilities that must be staffed even after deployment of an extinguishing agent. Numerous mission-critical military situations have the same requirement. Current commercial halon systems are employed to protect ground-based radar and military command and control centers, such as those on Navy ships, as well. Similar systems, which are designed to suppress fires and explosions in armored vehicles during combat, are also in place.

The use of the current commercial halons for the requirements mentioned above, as well as numerous others, has become very widespread during the past two decades. Fixed suppression systems number in the thousands. There are even more portable extinguishers in use, making halons an integral part of fire protection engineering. As such, they currently play a crucial role in the protection of national resources and national security of the United States. The same is true for other industrialized countries.

2. The Search for Halon Alternatives

The discussion in the last section suggests that the manufacture of the current commercial halons is likely to be phased out by the year 2000. On June 21, 1988, E.I. du Pont de Nemours & Co., a major manufacturer of halon 1301, announced plans to initiate just such a phaseout [9]. Other companies have announced that production will cease as soon as safe alternatives are available [19].

The fire protection community has recognized the seriousness of the situation. In 1987, an International Halon Research Project (IHRP) was initiated under the auspices of the National Fire Protection Research Foundation to conduct collaborative research [9]. The IHRP has released two reports [20,21] designed to be first steps toward reducing releases of halon 1301 into the atmosphere. A project designated as the "Best/Essential Use Project" was initiated by IHRP at the beginning of 1989. This project is designed to identify applications where commercial halons are currently employed which can use alternative fire protection methods [9].

Some essential fire protection needs cannot be met by existing alternatives to the current commercial halons. Users of such systems have recognized the seriousness of the situation and have begun to take action. Organizations are being formed to guide the search for alternatives which are effective fire suppression agents and have other desirable properties of the current commercial halons, but which do not pose a significant threat to stratospheric ozone.

One of the first steps in this process was a meeting organized by the United States Air Force and the Environmental Protection Agency, which was held at Tyndall Air Force Base in late 1988 [22,23]. Numerous presentations were made delineating the problems faced, establishing the current understanding, and identifying available resources. The participants recognized the need for the development of new agents and a cooperative effort between private and public research interests was suggested as a mechanism for accelerating the development of new chemicals. Recommendations were provided for research areas to serve as the basis of a comprehensive plan.

During the past year, the Halon Alternatives Research Corporation (HARC) was established by the private sector to foster efforts to develop alternatives. A government working group has been formed to serve as liaison between HARC and Federal agencies. Efforts are moving forward to implement an effective research plan. Reference [19] discusses these efforts.

In the meantime, a comprehensive research plan for identifying suitable replacements for the current commercial halons has been formulated by an ad hoc technical committee as an outgrowth of the Tyndall meeting [24]. The project described in this report is an element of this plan.

C. SCOPE/APPROACH

1. Nature of the Problem

The current commercial halons are likely to become prohibitively expensive or totally unavailable for fire suppression and inerting purposes by the year 2000. There is a clear requirement for replacement chemicals which have the following properties: fire suppression effectiveness, low toxicity, low residue, favorable physical properties, low electrical conductivity, and materials compatibility. At the same time, these chemicals must be far less destructive to stratospheric ozone than the halons which they are expected to replace. Unfortunately, since the current commercial halons were thought to possess ideal properties, there have been very few research efforts since the late 1940s designed to identify alternatives. The last wide-ranging study was that carried out by the Purdue Research Foundation [25] during the late 1940s with support from the U.S. Army Engineers Research and Development Laboratories. (Even this study focused primarily on fully halogenated compounds.) As a result, very little research infrastructure and scientific expertise exists for the search.

As discussed in Section II.C.1, the unusual chemical stability of the halons contributes to their effectiveness as fire extinguishing agents. Unfortunately, it is this same chemical stability which allows these chemicals to pass unreacted through the earth's troposphere and penetrate the stratosphere. The culmination of this process is the catalytic destruction of stratospheric ozone by bromine atoms which are produced in the photolysis of halons (see discussion in Section II.C.3). The development of new fire suppression agents which have the desirable properties of the current commercial halons but which are less harmful to stratospheric ozone will probably require careful balancing of chemical reactivity behavior. Principles need to be developed to identify the best possible alternatives.

Two general search strategies for alternatives are immediately obvious. One approach is to consider chemical modifications of the commercial halons such that their fire suppression capability is maintained, but their atmospheric reactivity is increased to the point where transport to the stratosphere is minimized. The second approach is to identify completely different chemical families which offer the required characteristics. A wide-ranging search must incorporate both approaches.

2. Structure of the Research Program

Under U.S. Air Force sponsorship, the National Institute of Standards and Technology (NIST) has undertaken to identify approximately 100 compounds covering a range of chemical and physical properties believed to affect flame suppression capability. Following a thorough literature search, NIST staff members have devised a strategy for identifying these compounds. This report serves to document the existing knowledge of fire suppression, the search strategy employed, and the physical and chemical properties of the compounds which have been chosen for consideration.

3. Search Strategy

The first priority of this project was to define the boundaries for the search. No systematic search for new flame suppressants has been done since the late 1940s. We did a thorough literature search to define the current understanding of flame suppression. This understanding serves as the foundation for the remainder of the project.

The next task was the identification of chemical families to be considered. The decision was made to consider as wide a range of chemical families as possible. As a result, chemicals which have been investigated in the past for fire suppression effectiveness were identified and assessed. The search was then expanded to include classes of chemicals which have not been considered for fire suppression purposes previously.

Several different approaches were possible for the search. One was to identify the compounds offering the best possibilities as short-term alternatives for the current commercial halons. The project team quickly realized that the existing knowledge of fire suppression, ozone depletion, toxicity, and other physical properties was insufficient. An alternate strategy was to choose compounds in such a manner that the principles necessary for the selection of alternatives for the current commercial halons would be tested. These principles would then be available to guide future work. An intermediate path was ultimately chosen. As a result, the final list of compounds contains members which are likely to be among those agents chosen in the near future for further testing as alternatives for the current commercial halons. At the same time, other molecules which are definitely not suitable for replacing these halons are included to allow the development of the principles required to guide the search for the best possible alternatives. This approach facilitates both short- and long-term efforts to find the best possible alternatives for the current commercial halons. The intention was to develop a broad base of knowledge to aide researchers and manufacturers in responding to future changes in the regulatory environment.

Next, we decided upon a method to weight the various properties which make the current commercial halons so effective for fire suppression purposes. These properties are listed in the first paragraph of this section. We decided to focus on two:

- fire suppression and inerting, the principal functions of these agents; and
- stratospheric ozone impact, the principal reason the future of these chemicals has come into question.

The project team realized that the decision to focus on fire suppression and ozone depletion required that several other important characteristics be deemphasized. Perhaps the most crucial of these is toxicity. Clearly, one of the most important characteristics of existing agents is that they can be deployed effectively in the presence of people. This is a result of their relatively low toxicity. Unfortunately, toxicity cannot be predicted confidently from chemical structure. Generally, the toxicity of a particular chemical is determined by a battery of expensive and time-consuming tests. The approach taken for this study is to report existing toxicological data for compounds included on the final list, but not to attempt to predict the toxicological behavior of compounds for which no previous studies are available.

Some general guiding principles for toxicological behavior are known (e.g., compounds containing fluorine tend to be less toxic than their iodine analogs) and have been incorporated into discussions of the chemical families which appear later in the report. Compounds which are known to be toxic, and in some cases highly toxic, are included on the final list. These compounds are not considered to be viable alternatives for the current commercial halons (even though certain limited uses as fire suppressants are possible for some) but are included to test principles of fire suppression or ozone depletion.

The toxicity referred to above is that for the chemicals themselves. Another important consideration is the toxicity of decomposition products which results from the deployment of an agent on fires or in other heated environments. Numerous discussions of this topic (e.g., references [6,26,27,28,29,30,31,32]) with regard to the current commercial halons indicate that hydrogen halides, halogens, and other halogenated compounds are formed. All of these compounds are noxious and toxic at relatively low levels. These species can also damage a wide range of materials and cripple electronic equipment.

These dangerous combustion products do not usually pose serious toxicological and materials problems when the current commercial halons are deployed for fire suppression. This observation is traced to the effectiveness of these fire extinguishment agents. If properly applied, the fire is extinguished so rapidly that only small concentrations of these products are created [27,29,31]. Observed levels of fire products attributable to the use of these agents are usually not dangerous. Certain situations involve exposure of the current commercial halons to deep-seated fires [28] or hot appliances [31] where high levels of noxious gases can be formed by decomposition of the agents. Conditions where the combustion products resulting from usage of the current commercial halons pose a realistic danger have not been investigated extensively and no quantitative results were identified during the literature search.

The combustion products generated by the application of alternative compounds are not likely to be more toxic than those generated by the use of the current commercial halons. It is further assumed that any replacement agents will have roughly similar fire suppression effectiveness. On this basis, it can be concluded that toxic products generated by the use of alternatives will not represent a more significant threat than those resulting from the use of the current commercial halons. While recognizing that a potential problem exists, the likelihood of producing toxic products during fire suppression has not been considered in choosing the chemicals included on the list.

Ideal alternatives for the current commercial halons would be "drop-in" agents. In other words, the physical and materials compatibility of the replacements would be such that they could be used in existing halon suppression systems. This criterion is much too confining for a wide-ranging search for alternatives. Some general selection of physical properties is enforced by requiring that compounds on the list be gases or easily vaporizable liquids, but compatibility with current commercial halons is not included as a criterion. Even the simple requirement of being a liquid or gas is waived for a few compounds.

Generally, compounds which are gases or vaporizable liquids will leave no residue if pure. The electrical conductivity of most gases and liquids is low, but no attempt has been made to consider this property in the search strategy. Materials compatibility is very important for the design of practical fire suppression systems. Nonetheless, it was decided that consideration of this property should also be deferred and it was not used as a criterion for including compounds on the list.

4. Report Philosophy

a. Breadth of Coverage

This project is intended to be comprehensive. The current understanding of fire suppression and ozone depletion is utilized to choose approximately 100 compounds for testing purposes. A summary of this understanding is provided to give the reader the needed background to evaluate the basis for recommendations which are made. Large numbers of references to original literature are provided to allow readers to obtain additional details.

We have generated a detailed report which we hope will capture the current understanding of the problem, give clear explanations of approaches utilized in the study, and provide a comprehensive document which can serve as the basis of the search for alternatives to the current commercial halons. As much detail as possible is provided for each chemical species included on the list to aid researchers who might test or evaluate these chemicals in the future.

b. Report Structure

The report is divided into 4 major sections. This section began with a statement of the objective of this study. Next, the properties of the current commercial halon fire extinguishing agents were enumerated with regard to their composition, historical development and uses. In the following subsection, the relationship of this project to other ongoing efforts is discussed.

Section II is devoted to providing an overview of relevant areas of combustion science. Included are descriptions of the current understanding of fire suppression mechanisms, various approaches which are utilized for testing flame suppression effectiveness and a brief introduction to the mechanisms by which the current commercial halons are thought to contribute to the depletion of stratospheric ozone.

Section III is divided into subsections corresponding to the chemical families which were considered in this investigation. A justification for including each chemical family, as well as a discussion of previous tests of family members for fire suppression effectiveness, is presented. Recommended compounds from each chemical family are tabulated, along with relevant properties, following each subsection.

The conclusions of this investigation are presented in Section IV along with the complete exploratory list of chemical alternatives. Separate data sheets for each of the compounds on this list are included in an appendix.

5. Relation of This Work to Other Efforts

The Engineering & Services Laboratory of the U.S. Air Force is funding a number of research efforts related to usage of current commercial halons and alternatives. The goals are to provide a short-term reduction in halon releases and a long-term solution to the problem by identifying appropriate alternatives for training and use. An effort has been underway at the New Mexico Engineering Research Institute (NMERI) for several years [33]. This program has primarily considered means for reducing releases of the current commercial halons to the atmosphere and the replacement of these halons with close chemical relatives and mixtures.

The National Institute of Standards and Technology (NIST) is performing three projects--"Construction of an Exploratory List of Potential Replacements for halons 1211 and 1301," "Preliminary Screening Procedures and Criteria for Replacements for halons 1211 and 1301," and "Halon Candidate Agent Database." The team members of these three projects have interacted closely so there is a great deal of coordination between these efforts.

It is anticipated that the compounds included on the master list will be passed through the preliminary screening procedures under development at NIST. This initial screening will serve as a highly effective test of the screening process and will generate initial information with regard to the relative ordering of the compounds in terms of screen properties. Careful experimentation will be required to more fully develop the fire suppression and ozone-depletion principles which the list of compounds has been explicitly chosen to test and verify.

The database project has been the source for many of the physical properties included in this report. At the same time, many of the compounds identified in the current research effort will be included in the database. Some of the findings of the literature search for this work will also be added to the database.

The United States Environmental Protection Agency is funding a project entitled "Examination of Fire Types" which is being performed by Factory Mutual Research Corporation of Norwood, MA. This project is designed to identify the classes of fires for which the current commercial halons are used and recommend generic fires for testing purposes. The results of this project will be used for practical fire testing of compounds identified as the most likely candidates as alternatives for the current commercial halons.

SECTION II

CURRENT UNDERSTANDING

A. COMBUSTION AND FIRE CONCEPTS

This Section reviews the fundamental concepts of combustion and fire required for understanding the discussion on fire suppression and inerting as well as the literature discussed during the remainder of the report. The approach taken is intentionally introductory and many details are omitted. Any of several excellent texts on these subjects (e.g., [32,34,35,36,37]) can be consulted for more in-depth treatments.

1. Definitions of Combustion and Fire

"Combustion" and "fire" have general meanings which are recognized by everyone. At the same time it is difficult to provide specific definitions. For the purposes of this report, combustion will be defined as "a rapid and persistent chemical reaction which combines fuel and oxygen to produce heat and light." The quotation is adapted from an introductory book by Cottrell [38].

The above quotation was provided by the author to define fire and not combustion. Generally, a more restrictive definition, such as that provided by Berl [39], is used for fire. Fires are "special cases of combustion where the addition of fuel and oxidizer to a flame is not under human control" [39]. The class of fires of interest for this report are uncontrolled and unwanted fires. These fires are generally harmful, destructive, and/or dangerous.

2. The Fire Triangle

The fire triangle is an introductory concept often employed to remind readers of the three conditions which must be present simultaneously for combustion to take place and sustain itself. These requirements are fuel, oxygen, and heat. These are often drawn along the sides of a triangle to emphasize that all three are required.

The fire triangle also provides insights into how fires can be suppressed. If any of the sides of the triangle is removed, the fire will be extinguished. This will become clearer in the section on extinguishment mechanisms.

3. Combustion and Fire Classifications

Numerous methods are used to classify types of combustion and fire. A few of these are mentioned to provide background and nomenclature for the discussions which follow.

a. Flaming Combustion and Smoldering

Two types of combustion are common in fires. The first is known as flaming combustion and involves chemical reactions occurring primarily in the gas phase. The name arises from the fact that the combustion is characterized by the emission of visible and infrared (heat) electromagnetic radiation by the fire. These emissions are the means by which a person often detects the presence of a fire. The visible radiation is either (a) emission from electronically excited chemical species formed as the result of the chemical reactions or (b) thermal radiation from small particles (soot) located in regions of high temperature which obey Planck's black body radiation law.

The second type of combustion is only important for burning solids such as wood or plastics and involves chemical reactions occurring directly at, or near, the surface within a solid. These are heterogenous reactions since the solid surface reacts directly with oxygen from the surrounding gases. This process is known as smoldering.

Flaming combustion is usually more vigorous and generates higher temperatures than smoldering. As a result, flaming combustion is often more dangerous and poses a more immediate threat. On the other hand, smoldering can generate significantly higher concentrations of toxic gases than flaming combustion (this depends on oxygen availability) and can be more difficult to extinguish. Smoldering often evolves into flaming combustion.

b. Fuel Types

One example of fire classification based on fuel type is given in the footnote at the bottom of page 2. This scheme is employed to allow people who must control these types of fires to rapidly identify a fire class and to determine the best available means for firefighting.

Combustion processes can also be classified based on the normal state--gas, liquid, or solid--of the fuel. This classification is important because it determines the mechanisms by which the fuel is made available for flaming combustion. Note that liquids and gases do not support smoldering combustion under normal conditions.

For gases, the fuel is provided directly to the combustion region. An example is the flow of natural gas to a laboratory Bunsen burner. The supply of gaseous fuel is determined simply by the gas flow rate.

Liquid fuels are considerably more complex. Burning conditions for liquid fuels can vary. As an example, consider the common configuration of flaming combustion occurring above a pool of the liquid fuel. The gaseous fuel results from vaporization from the liquid surface, and the fuel supply rate is determined by the rate of fuel vaporization and the surface area of the pool. The vaporization rate per unit area is highly sensitive to the liquid temperature and the radiation flux from the fire. Since flaming combustion can heat the liquid by thermal conduction, convection, and radiation, it is possible for the flames to affect the vaporization rate, and the fire can therefore influence its own behavior.

Combustion involving solid fuels is by far the most complicated. Here, the heat feedback from the overhead flames is crucial for generating the gaseous fuels required for flaming combustion. In some cases a solid fuel can simply melt and produce a vaporizable liquid which burns as a pool fire. More generally, however, complex pyrolysis and chemical reactions occur near or at the solid surface resulting in the release of gaseous products which serve as the fuel. These processes can result in even more complicated behaviors in the solid such as charring. Wood burning is a common example of this type of combustion.

c. Premixed and Diffusion Flames

These terms refer to the means by which the fuel and oxidizer are mixed. When the fuel and oxidizer are mixed before combustion the flames are known as premixed. A flame propagating down a tube containing a mixture of a hydrocarbon fuel and air is an example of a premixed flame. A diffusion flame is one where the fuel and oxidizer are not premixed, and the combustion and mixing take place at the same position(s). Common means for mixing are molecular or turbulent diffusion, hence the name. A candle is an example of a diffusion flame, where the combustion is the result of molecular diffusion of fuel and oxidizer species.

It is possible to have intermediate cases between premixed and diffusion flames. A Bunsen burner allows partial premixing of fuel and air, but the amount of air provided by the burner may be insufficient for complete combustion. In this case, additional reaction between excess fuel and ambient oxygen occurs.

d. Laminar and Turbulent Combustion

For gas-phase combustion, the behavior of the flow field is central to the flame characteristics for both premixed or diffusion flames. Gas flows are typically characterized as laminar or turbulent, and, while a complete discussion of these effects is beyond the scope of this report, a few general comments are necessary. Here we follow the discussion of Fox and McDonald [40].

These classifications of flow are based on macroscopic behavior. In laminar flow, there is no mechanical mixing between adjacent layers of the fluid. The flow is "smooth." The only dispersive mechanisms are the result of molecular diffusion. By contrast, turbulent flow is characterized by the generation of numerous and apparently random velocity fluctuations. These velocity fluctuations are the result of the formation of vortices extending over a wide range of size scales. These motions provide a mixing mechanism for adjacent layers of fluid. As a result, transfer and mixing of momentum, heat, and mass is much greater for turbulent flows than observed in laminar cases.

The type of flow which occurs is sensitive to a large number of system parameters. In general, small area flows at low velocities will be laminar. An example of a laminar flame is a small candle. As the area of the flow or its velocity increases a transition to turbulent behavior occurs. Most fires covering areas greater than a few centimeters involve turbulent combustion.

As might be expected, the behaviors of combustion systems involving laminar and turbulent flows are different because of large variations in the rates of temperature, chemical species, and momentum mixing.

e. Lean, Stoichiometric, and Rich Combustion

These terms refer to the relative amounts of fuel and oxidizer available for combustion. When the amount of oxidizer is exactly that needed to convert all fuel to final products (CO_2 and H_2O for most fuels) the combustion is said to be stoichiometric. If excess air is available, the combustion is lean, and in the opposite case, (fuel in excess), the combustion is rich.

4. Basic Combustion Concepts

The attempt to understand combustion is a part of the earliest of modern scientific research [41]. The complex nature of the interaction between the flow fields and the chemistry made progress difficult. However, today the major elements of the problem are understood and modeling calculations provide reasonable results for simple combustion systems.

a. Thermodynamics

Combustion occurs when a fuel and an oxidizer (typically air) mix and are ignited. The resulting reaction generates heat and light. Thermodynamics provides the tools to calculate the amount of heat which can be released for any given fuel. It also allows the calculation of the maximum possible temperature which can be generated by a flame and the equilibrium concentrations of species which are produced. As an example, consider the combustion of the simplest hydrocarbon--methane. The overall reaction of methane with oxygen can be written as

$$CH_4 + 2O_2 \rightarrow 2H_2O + CO_2.$$

The heat of reaction at room temperature is calculated as the sum of the standard heats of formation for the products minus that for the reactants. The net heat release for the above reaction is 802 kJ/mole of CH_4 consumed. This quantity, the heat of reaction of fuel with oxygen to produce water and carbon dioxide, is called the heat of combustion. Similar calculations can be made for any fuel, whether it is a simple gas (as above) or a complex fuel such as wood.

The heat of combustion can be used to estimate the maximum temperature a flame can achieve. This is called the adiabatic flame temperature. To calculate this quantity, it is necessary to know both the heat of combustion of the fuel and the composition of the reaction mixture. When methane is burning in air, this means that we must account for the nitrogen, which does not take part in the reaction. In addition, it must be assumed that all of the heat released by the combustion reaction goes into heating the product gases and the nitrogen. Calculation of the adiabatic flame temperature also requires input of the heat capacities of all product and inert gases. The heat capacity of a gas is simply the number of joules that are required to increase the temperature of one mole of the gas one Kelvin. In general, the heat capacity of a molecule increases with increasing molecular complexity--the more atoms in the molecule, the more energy required to heat the molecule.

The calculation of equilibrium composition of the reaction mixture depends on the estimated flame temperature and requires knowledge of the heats of formation of stable species (such as CO), as well as, the heats of formation of the radicals having the highest concentrations in the flame (for example, hydrogen atoms, H; hydroxyl radicals, OH; oxygen atoms, O; hydroperoxide, HO_2; and methyl radical, CH_3). Finally, data on the entropy of formation for all of these species is needed. This process is iterated until convergence. These calculations can be extended to include other additives, such as inhibitors, provided that adequate thermodynamic data are available. The approximation of adiabaticity is generally good, but always produces an upper limit for the temperature. Equilibrium composition calculations are generally adequate if soot concentrations are not high. The data necessary for these calculations are, for the most part, well-known [42] and the calculations are readily performed.

Thermodynamics can be used to predict the amount of heat and the composition of the gases produced, but it does not address the question of how fast the reaction occurs. To do this it is necessary to examine the kinetics of combustion processes.

b. Chemical Kinetics

Combustion can be described as rapid oxidation. The yellowing of a piece of paper over time is an oxidation process as well, but it is slow. When a flame is touched to the same piece of paper, the resulting oxidation is much more rapid. The difference is the result of variations in the overall rates of reaction for the processes or, in other words, the kinetics. In the methane/air example given above, the fuel and oxidizer could have been mixed in a cylinder at room temperature and there would have been no reaction. On the other hand, even a small spark passing through the mixture would have initiated a rapid, indeed almost explosive, reaction.

To understand these differences in reaction behavior it is necessary to examine chemical kinetics in general, and, more specifically, the kinetics of ignition and propagation of flames. Overall reactions, such as the combustion of methane, generally occur by a number of individual reaction steps involving molecular species. These reaction steps are characterized by the reactants, the products, and the rate at which they occur. The reaction of H atoms and O_2 molecules to produce OH radicals and O atoms, an extremely important combustion reaction, is written as

$$H + O_2 \rightarrow OH + O.$$

The rate at which the reaction occurs can be defined in terms of the rate of loss of a reactant, $-d[H]/dt$ or $-d[O_2]/dt$, or the rate of production of a product, $d[OH]/dt$ or $d[O]/dt$. (The notation [X] denotes the concentration of X in moles/volume.) The reaction rate is equal to the product of the reactant concentrations times a rate constant, k,

$$\text{Rate} = k[H][O_2],$$

where the rate constant is usually expressed as

$$k = AT^n \exp(-E_a/RT).$$

The energy of activation, E_a, is a measure of the energy barrier that the reactants must overcome to produce products. The preexponential factor, AT^n, incorporates the rate of collision between the reactive species in the gas phase and the probability that if the reactants have sufficient energy, reaction will occur. In general, most of the temperature dependence for a reaction step is the result of the energy of activation since it appears in an exponent. The form of the equation is such that for $E_a > 0$, the reaction rate increases with temperature. To understand why the methane/air mixture does not undergo combustion when mixed at room temperature, it is necessary to examine the details of the chemistry of combustion.

c. Combustion Chemistry

Combustion chemistry is primarily the chemistry of free radicals--their production, reaction, and destruction. A free radical is a molecular species that is very reactive because it contains unpaired electrons. These species are not generally thermodynamically stable at room temperatures -- they recombine to form stable molecules. At flame temperatures, typically > 800 K, their recombination (loss) processes are not as fast as their generation rate. Thus, the radicals' concentrations are relatively large, and their high reactivity dominates flame chemistry.

The most important free radicals in most practical flame systems are H and OH. In addition, CH_3, HO_2, and O are important in some situations. Beyond these species, dozens of other radicals play a role in the combustion of complex fuels. The chemistry of combustion is complex because of the very large number of species and because, at different temperatures and different ratios of fuel to oxidizer, different reactions among these species will dominate. We can characterize the major types of reactions in terms of their role in the overall chemistry. The usual classifications are:

- **Initiation Reactions.** These are reactions that provide the first radicals to start the combustion process for the fuel and oxidizer.

- **Branching Reactions.** These are reactions that increase the number of radicals and therefore the overall reaction rate. The most important of these reactions consume the oxidizer.

- **Propagation Reactions.** These reactions usually consume fuel or oxidizer with no net change in the number of radicals.

- **Termination Reactions.** These reactions reduce the net number of radicals or produce unreactive radicals from reactive radicals.

The branching reactions are common to all practical combustion systems. This is especially true for the branching reaction $H + O_2 \rightarrow OH + O$ discussed above. The individual initiation and propagation reactions often depend on the fuel. The important termination reactions are common to many systems.

Initiation reactions are typically like these:

$$H_2 + O_2 \rightarrow HO_2 + H$$

$$CH_4 + O_2 \rightarrow CH_3 + HO_2$$

$$C_2H_6 \rightarrow 2CH_3.$$

In these reactions, stable molecules react to generate radicals such as H and CH_3. These reactions typically have activation energies greater than 200 kJ/mol. These are the only reactions that produce radicals directly from the stable fuel and oxidizer. The high activation energies of these reactions mean that the rate constants, k, vary by over 30 orders of magnitude between room temperature and combustion temperatures. Even at combustion temperatures, these are typically slow reactions with rate constants below all of the other reactions we will discuss. To illustrate how slow these processes are, the reaction between H_2 and O_2 will produce less than one H atom per century at room temperature. Combustion does not occur unless the temperature is very high or there is some other source of radicals. Once the radicals are produced, the initiation reactions are completely unimportant; and the rate of reaction is set by the rates of the branching and propagation reactions.

The most important branching reaction for practical combustion systems is:

$$H + O_2 \rightarrow OH + O.$$

This reaction has an activation energy of 69 kJ/mole and an average pre-exponential factor. At combustion temperatures this reaction occurs about one in every hundred collisions. Most importantly, this reaction produces two reactive radicals, OH and O, for each radical (H atom) which is consumed. Reactions of O atoms with the fuel such as:

$$O + H_2 \rightarrow OH + H$$

$$O + CH_4 \rightarrow OH + CH_3$$

are also important. The OH free radicals produced by these reaction steps react primarily with fuel molecules in propagation reactions.

The propagation reactions are highly variable since they depend on the fuel type. Some examples are:

$$H_2 + OH \rightarrow H_2O + H$$

$$CH_4 + OH \rightarrow H_2O + CH_3$$

$$CO + OH \rightarrow CO_2 + H.$$

In each of these cases, the OH radical reacts with a fuel molecule (H_2,CH_4,CO) to produce a stable end product (H_2O,CO_2) and another radical (H,CH_3). All of these reactions have low activation energies (5-20 kJ/mol), although the third is an unusual reaction and is slower than the first two at flame temperatures. The propagation and branching reactions are typically fast reactions that, once started, will rapidly consume all of the available fuel or oxidizer.

The termination reactions either produce a radical with greatly reduced reactivity or produce stable products from two radicals. Examples are:

$$H + O_2 + M \rightarrow HO_2 + M$$

$$H + OH + M \rightarrow H_2O + M$$

$$CH_3 + CH_3 + M \rightarrow C_2H_6 + M$$

where in each case M is some third body that does not participate in the reaction, e.g, N_2. These reactions are typically slower than branching or propagation reactions at flame temperatures, but have negative activation energies, so that they become faster at lower temperatures.

It is possible to understand very simple combustion systems, such as H_2/O_2 within the context of a manageable set of reactions; and, for special cases, algebraic solutions of the rates of growth for the species involved can be found. In general, the reaction systems are so complex that computer modeling is essential just to understand the kinetics. When the effects of flow fields, mixing, and diffusion are included, even the simplest system must be modeled.

It is nevertheless possible to use the simple ideas discussed here to understand the general principles of combustion. For example, the stability of combustible materials at room temperature is a result of the high activation energies for their initiation reactions. The discussion thus far is only strictly applicable to simple gaseous fuels, but the same general features pertain to more complex fuels; that is, the initiation reactions which involve the creation of radicals from stable species will be slow at room temperature. In addition, the rate of combustion, once initiated, can be understood in terms of the branching and propagation reaction rates. The rates for branching reactions increase with temperature and are reasonably fast, and the radical attack on the fuel molecules is generally fast and has low activation energy. As a result, the overall reaction rate is sufficient to maintain combustion for high temperatures.

The same kind of analysis can be applied to the role of suppressants in the flame. To stop a combustion process one must either remove the radicals faster than the chain branching process can produce them (note that the propagation steps only maintain the number of radicals) or reduce the temperature so that the chain termination steps can dominate. These are really the same idea: in both cases the radicals are removed faster than the branching process can create them.

Consider, for example, the primary chain branching reaction

$$H + O_2 \rightarrow OH + O.$$

This reaction has an alternate channel,

$$H + O_2 + M \rightarrow HO_2 + M.$$

Both of these channels are always present. The second channel is pressure-dependent, that is the second order rate constant increases with pressure. The rate expressions of these two processes are such that at atmospheric pressure, the rates are roughly equal at 1000 K. Below this temperature the recombination channel (producing HO_2) dominates, while above this temperature the branching channel dominates. The $H + O_2$ reaction is also important since it is the predominant path for O_2 consumption in combustion. If there is competition for the

H atoms by other reactions, these will correspondingly reduce the net rate of the chain branching reaction by reducing the concentration of H atoms.

Using the ideas expressed here, it is also possible to see what role an ignition source plays in the combustion process. The rate of radical production by the initiation reactions is so slow that, at room temperature, the termination reactions will soak up any radicals faster than the branching reactions. If a sudden, concentrated local source of radicals is introduced, the branching and propagation reactions will produce enough excess energy to heat the gas locally and start the combustion. This local radical source could be a spark or a small flame. Once the combustion has been started, the problem of flame inhibition goes back to the same ideas discussed above. For simple combustion systems, H_2/O_2 or CH_4/O_2, the kinetic data is well enough established that modeling is a useful tool for analyzing the combustion process. Although there is some kinetic data on halocarbons and other halogens, it is inadequate for computer modeling of the flame suppression process.

d. Thermal balance

All of the concepts discussed above can be incorporated into the idea of thermal balance. The discussion above can be simply summarized as follows: the energy released in the combustion process must be sufficient to keep the temperature high enough so that the branching reactions can stay ahead of the termination reactions. The thermal losses, heating up new fuel and oxidizer and breaking the initial bonds, are made up by the thermal gains, exothermic production of combustion products. In a practical system there are other loss mechanisms such as radiation, conduction and convection that the exothermic processes must also make up. The heating of new fuel will, in a diffusion flame, also include the loss of H atoms to the fuel. This loss of H atoms can be viewed as a mechanism for self-extinction and is responsible for rich combustion limits.

These ideas can be translated into some simple rules of thumb for the limits of combustibility. For most organic fuels the heat of combustion is found to be approximately 425 kJ/(mole-O_2) [43,44,45,46,47]. Note that the mole-O_2 means per mole of O_2 consumed. Flammability limits, both rich and lean, and the limits in the presence of inerts have empirically been found to be expressed in terms of a limiting heat capacity for the reacting mixture (fuel/oxidizer/inert) of 210 J/(mole-O_2 K). That is, the mixture will not sustain combustion if the heat capacity of the mixture is greater than 210 J/K for each mole of oxygen present in the mixture [44,48]. Note that excess oxygen or fuel acts simply as an inert gas that adds to the heat capacity of the system. Thus, the addition to the heat capacity of the mixture can be accomplished by the addition of an inert, excess fuel, or excess oxidizer. The heat production is constant per mole of O_2 consumed, so the increase in heat capacity must correspond to a decrease in the final temperature of the flame. The result is again the dominance of the recombination processes over the branching process.

The use of the ideas of chemical kinetics can provide a qualitative understanding of the rationale behind thermal balance, but the results depend on the fluid mechanical details of the combustion and must be determined either from experiments or from models that mimic the system under consideration. To the extent that there are other loss mechanisms for the radicals needed for the branching reaction, the simple ideas developed from the thermal balance will not hold. Thermal balance concepts have been extended to include the definition of a limit temperature. That is mixtures having an adiabatic flame temperature below some lower limit will not support combustion. These temperatures have been found to be greater than that for which the rates of the branching and recombination channels of the $H + O_2$ reaction intersect for a wide variety of combustion systems. This suggests that additional radical loss mechanisms are operant.

e. Propagation Rates of Premixed Flames

An important property for a burning fuel/oxidizer system is its flame speed. This property is generally only meaningful for gaseous and liquid fuels for which flammable gaseous mixtures can be formed. There are a number of experimental methods available for flame spread measurements [49], but all attempt to report the one-dimensional flame propagation rate of the combustion front into the fuel/oxidizer mixture.

Flame speed measurements vary with a number of system parameters. As expected, flame speeds depend strongly on the concentrations of the fuel and oxidizer as well as the total pressure. Flame speeds are generally found to increase with the temperature of the unburned fuel/oxidizer mixture. In turbulent mixtures, flame speeds are proportional to both the turbulence intensity and the laminar flame-spread rate [50]. The majority of all flame speed measurements are reported for fuel/air mixtures at ambient atmospheric conditions.

f. Flame Structure

The term "flame structure" refers to the details of the velocity, temperature, and concentration fields in the vicinity of the combustion reaction zone. The structures for both premixed and diffusion flames are characterized on the basis of experimental measurements. Usually, well-defined systems are investigated in which the combustion region can be assumed to be one-dimensional. Thus far, most interest has focused on laminar flames. Interactions of the heat release of combustion with the turbulent motion of fluids, along with temporal fluctuations of properties, makes flame structure determinations in turbulent flames very difficult. It is significant that the most widely accepted theoretical treatment of turbulent combustion--the laminar flamelet approach [51,52]--treats the local flame structure in a turbulent flame as being a laminar flame.

Modeling of combustion and diffusion flames involving full-kinetic treatments of major chemical reactions [53] and realistic treatments of molecular diffusion transport [54] allows flame structures to be calculated for simple laminar fuel/oxidizer systems. In general, excellent agreement is obtained between experimental and calculated results.

B. INTRODUCTION TO FIRE SUPPRESSION

This Section is intended to serve three purposes.

- First, the current understanding of fire suppression is summarized. The goal is to help the reader to understand why and how choices were made concerning the compounds included on the final listing.

- Second, the types of experiments used to characterize fire suppression effectiveness are summarized. This discussion provides the understanding necessary to evaluate past measurements of the fire suppression capabilities for compounds included on the list.

- Third, the results of past measurements are used to determine whether (or not) chemical fire suppression is a general phenomenon. This is important since many of the chemicals included on the final list are intended to test various principles concerning chemical mechanisms for flame suppression. Experimental findings strongly suggest that combustion suppression can occur by chemical pathways.

1. Relevant Reviews

There are numerous literature reviews and critical analyses of fire suppression. These should be consulted by any reader interested in developing a basic understanding of the field. Some of these reviews are mentioned here as a guide for the reader.

An excellent review of early work was provided by Fryburg [55]. This work considers fire suppression mechanisms in general, but focuses on the possibility of chemical suppression. A contemporary report prepared by Malcolm [56] is not a review article per se, but it does provide an invaluable summary of a number of investigations dealing with fire suppression and halogenated suppressants. In 1957, a thorough review of flame suppression mechanisms by Friedman and Levy [57] appeared. This review was followed by two shorter efforts designed to summarize the literature appearing during interim periods [58,59] and two additional short reviews [60,61]. Other authors have contributed to the interim reviews and a continuous record can be traced up through 1969 [62,63,64,65,66]. The monograph edited by Gann is an invaluable source of information on various aspects of flame suppression and the halogenated fire suppressants in particular [67]. A bibliography of halon literature up through 1976 has been prepared by Miller and Kenney [68].

More specialized reviews are also relevant. Workers at the U.S. Bureau of Mines have provided extensive reviews and critical analysis of flammability data for gases and vapors [69,70]. A later review dealing with the same subject includes a section on flame inhibition [71]. Two authors have provided extensive reviews with a focus on the reactions important for flame suppression chemistry [72,73].

No reviews of this field have appeared since 1976 because very little new data have been reported after this date. Most of these additional studies will be discussed during the following sections. The dearth of recent studies can be traced directly to the success of the current commercial halons as fire suppressants. Their properties have been so well-suited to their use that there has been little incentive for improvement; as a result, research funding for this area had dried up.

The lack of recent research in fire suppression suggests that it may be possible to make rapid progress. During the past 15 years, significant gains have been made in the understanding and modeling of combustion systems. These advances are available to researchers and should be directly applicable to the problem of flame suppression.

2. Fire Suppression Mechanisms

The possible mechanisms of flame suppression can be categorized in various ways. Here we follow the discussion of Friedman and Levy [57], but their discussion is typical of other authors. Two general classes--physical and chemical--for flame extinguishment mechanisms are recognized.

a. Physical Fire Suppression Mechanisms

There are 4 types of physical fire suppression mechanisms. Brief introductions to each are provided. Reference to the fire triangle discussed earlier in section II.A.3 provides immediate insights into the physical basis for these processes.

- **Smothering or Blanketing.** This physical mechanism operates by separating the fuel and air. Covering a small fire with a blanket to extinguish it is a common example. Application of appropriate gases and liquids can also smother a fire. Carbon dioxide fire extinguishers are recognized as operating primarily by blanketing.

- **Cooling and Dilution.** These processes absorb heat from the combustion zone and lower the temperature. As discussed in section II.A.4.d, it is possible to extinguish a flame when sufficient heat is extracted. There are a number of physical means by which heat can be absorbed by agents added to a fire. These include simple heating of the agent (proportional to the heat capacity), phase changes such as vaporization or sublimation, and endothermic decomposition. One might also expect that the rate of heat transfer from the combustion zone, as well as the heat capacity, might be an important parameter for cooling mechanisms. The physical property which characterizes heat transfer behavior is thermal conductivity. The results of experiments suggest that the dominant physical property is heat capacity and that thermal conductivity plays only a minor role in flame inhibition.

- **Mechanical Means.** This term refers to mechanisms by which the fuel, heat, and/or air are forcibly separated. For example, blowing on a match removes the heated gases and soot necessary for sustaining combustion from the flame zone and extinguishes the flames.

- **Flame Radiation Blockage.** Friedman and Levy [57] also discuss a mechanism by which flame suppression occurs when an agent is interposed between the surface of a liquid or solid fuel and the flames which absorbs the thermal radiation which is necessary for the generation of gaseous fuel. Very little discussion of this process is found in the literature.

b. Chemical Fire Suppression Mechanism

This classification refers to an agent, which either by itself or through its decomposition products, interferes with the combustion chemistry to a degree sufficient to inhibit (or suppress) combustion. Based on the current understanding of combustion as consisting of chain reactions, the most effective chemical inhibitors would be expected to be those which remove chain carriers in, or near, the reaction zone.

c. Chemical Fire Suppression and Physical Cooling

When a chemically active agent is added to a combustion system the agent will have both physical and chemical effects. The concept of chemical fire suppression was suggested when agents were identified which were more effective fire suppressants than expected based simply on their physical properties. Only very recently have efforts been made to quantify the contributions of physical and chemical modes of fire suppression for an agent. Such studies are discussed in Section II.B.4.b.

The relative effects of cooling and chemical effects on the suppression of a fire are difficult to ascertain, in part, because the details of the heat removal processes are not well defined. Consider a diffusion flame. Based on existing combustion models it is expected that the location where temperatures must be lowered in order to cause flame suppression is in the vicinity of the high-temperature flame zone. This zone transfers heat to its immediate surroundings, and the process continues until the temperature reaches that for the surroundings. No definitive prescriptions are available for handling the different heat transfer processes implied by this discussion. For instance, room temperature heat capacities are sometimes used for correlating flame suppression efficiencies, while others use an integrated heat capacity from room temperature to some assumed flame temperature. For evaporation or endothermic decomposition, the location of the process relative to the combustion region might be expected to be very important. No analyses are available which treat this problem. Similar considerations will apply to premixed flames.

A concept which has been used implicitly in the discussions above requires further explanation. Simple endothermic thermal decomposition has been treated as a heat extraction mechanism capable of cooling a flame. It is therefore classed as a physical mechanism for flame suppression, despite the fact that thermal decomposition is recognized as a chemical process. Thermal decomposition is defined to contribute to chemical flame suppression only if it generates a chemical species which interferes with the combustion chemistry. Two hypothetical examples serve to illustrate this point. Consider an agent capable of undergoing endothermic decomposition to produce two inert molecular species. The flame would be cooled by the heat capacity of the agent as it is heated, the heat absorbed during the thermal decomposition of the agent, and any additional heat absorbed by the inert species which are generated. Since the species which are generated by the thermal decomposition are inert, only a physical mechanism is considered to be active. The alternative case occurs when thermal decomposition produces one or more molecular species which are reactive and capable of interfering with combustion intermediates and inhibiting the flame chemistry. Both physical and chemical mechanisms are active in this case. Heat absorbed from the flame system by the agent, the agent's thermal decomposition, and the decomposition products would be classed as a physical mechanism. Only the inhibition of the flame chemistry as the result of the active species generated by the decomposition is classed as a chemical mechanism of fire suppression. Fire suppression in the latter case is the result of both physical and chemical mechanisms.

3. Characterizations of An Agent's Flame Suppression Capabilities

There are fundamental justifications for investigating flame suppression, but for the purposes of this report, the principal objective is to identify agents which are effective as fire suppressants for unwanted fires. As a result, the ultimate test of an agent is its ability to extinguish fires which are characteristic of real unwanted fires. Note that these will usually be relatively large, turbulent diffusion flames.

Cost, material, and time limitations prevent testing every possible agent on a full-scale fire. As a result, numerous procedures have been developed which are designed to provide guidance to researchers in characterizing fire suppression behavior. These tests range from observations of flame structure changes in premixed flames to full-scale fire tests. The descriptions which follow provide the necessary background to understand the significance of previous tests of fire suppression agents. The methods are listed in a rough order such that their relevance to actual fire situations is increasing. Note that measurements in premixed flames are directly applicable to situations where the agent is employed to inert fuel-air mixtures. Nonetheless, diffusion flame investigations are deemed more relevant for extinguishment of unwanted fires.

a. Flame Chemistry and Flame Structure of Premixed Flames

In these experiments, the fuel and oxidizer are premixed and burned in the presence and absence of an added agent. It is possible to monitor the combustion products of the reaction and see if the agent undergoes a chemical transformation. An example of such an investigation is the work of Burdon et al. [74], who found that bromine and hydrogen bromide were produced when hydrogen and carbon monoxide were burned in the presence of methyl bromide.

In a series of benchmark papers, Biordi and coworkers [75,76,77] have reported detailed concentration profiles for low-pressure premixed flames of methane, oxygen, and argon in the absence and presence of low concentrations of CF_3Br. These investigations have provided important insights into the chemical mechanisms of flame suppression.

b. Agent Effects on Flame Speed of Premixed Flames

Flame speed, or burning velocity, is the rate at which the combustion front moves into a premixed fuel and oxidizer mixture. Burning velocities are experimentally determined in a variety of ways [49]. The velocities observed are sensitive to parameters such as the fuel/air ratio, temperature and pressure. The addition of fuel additives also modifies the burning velocity. A decrease in burning velocity with the addition of varying amounts of flame suppressants is sometimes employed as a measure of flame suppression capability.

An early example of such an investigation is the work of Rosser et al [78]. These researchers reported the effects of a variety of agents on the flame speed of methane-air flames. Several of these compounds contained bromine atoms. A very good correlation was found of the effect of an agent on the flame speed and the number of bromine atoms contained in the agent. Ratios of inhibition effectiveness for Cl:Br:I were reported as 1:7:7.

Lask and Wagner [79] reported the effects of a number of additives on hydrogen and hydrocarbon flames. Data are reported graphically for flame velocity versus percentage of added agent as well as in tables with the percentage of additive required to reduce measured flame speeds by 30 percent. One of the most interesting observations was that bromine-containing molecules reduced flame velocities much more efficiently than those containing chlorine. Limited measurements on species with iodine suggested that this atom was still more effective. This observation was confirmed by Halpern [80]. A comparison of the effects of several halogenated hydrocarbons on the flame speed of methane/air mixtures showed that compounds containing bromine were considerably more effective than those containing chlorine.

Homann and Poss [81] measured the flame speed of ethylene/air flames inhibited with a series of compounds as a function of pressure. Pressure was varied from 18 kPa to 101 kPa (101 kPa is one atmosphere). As expected, flame speeds varied substantially with pressure. However, when data for inhibited flames were normalized by the flame speeds for uninhibited flames, the results for different pressures collapsed into a single curve. An interesting observation of this work was that CH_3I was slightly more effective as a suppressant than CH_3Br at both high and low pressures.

c. Agent Effects on Premixed Flame Flammability Limits and Peak Concentrations

Flammability limits refer to the relative amounts of fuel and oxidizer in the mixture necessary to sustain combustion. These measurements are often made in a device called an explosion burette. The mixture to be tested is placed in a long tube, open to the atmosphere with sufficient diameter to ensure that the walls have a minimal effect. A spark or small flame is used to ignite the gases. The mixture is considered to be flammable when the combustion propagates to the end of the tube and nonflammable when propagation does not occur. By varying the concentrations of the gases it is possible to map out the flammability curve. Other devices utilized for determining flammability diagrams are discussed by Ford [2].

The effect of an agent on combustion behavior is often characterized in terms of the lean and rich flammability limits as the concentration of the additive is increased. Usually the concentration range of fuel and air capable of supporting combustion decreases as the agent is added. Extensive compilations of flammability results are available [69,70]. The work of Moran and Bertschy is also of interest since they investigated the flammability limits of pentane/air mixtures for a number of halogenated hydrocarbons [82].

As the agent concentration is increased, a point is reached where the lean and rich limits coincide. The agent concentration at this point is called the flammability peak concentration or, more simply, the peak concentration. Further increases in agent concentration lead to a situation where the fuel and air will not support combustion for any fuel to air ratio. Peak concentrations are often used to rate agent effectiveness. The most extensive series of measurements have been provided by the Purdue Foundation [25]. Results are provided for 56 compounds.

d. Full Kinetic Modeling of Premixed Flames

In recent years, it has become possible to model important aspects of laminar flames. This does not imply that complete modeling of combustion systems is feasible. Soot formation, for example, remains an intractable problem. However, equations which include realistic treatments of mass, momentum, and heat transfer, and which incorporate complex kinetic mechanisms to treat the chemical reactions, can be solved. Frequently, these calculations are simplified by considering only one- or two-dimensional flames.

Numerous comparisons have shown that it is possible to accurately calculate laminar flame speeds and flame structures for a number of fuel/oxidizer systems. The significance of this advance cannot be overstated. It is now possible to make useful predictions concerning practical combustion systems on the basis of measured chemical properties (e.g., thermal conductivities and rate constants for individual reaction steps). Such understanding offers great possibilities for tailoring and modifying combustion systems to meet specific engineering goals.

A few workers have attempted to utilize these techniques for investigating flame inhibition. An early example of such an approach is a paper by Dixon-Lewis [83] in which the structure and properties for uninhibited and inhibited hydrogen/air premixed flames were investigated. These authors concluded that the primary mechanism of flame inhibition was the catalyzed removal of H atoms to form less reactive Br atoms by the reactions

$$H + HBr \rightleftarrows H_2 + Br$$

$$H + Br_2 \rightleftarrows HBr + Br.$$

Interestingly, the first of these reactions was found to be very close to partial equilibrium (i.e., equal reaction rates in forward and reverse directions), but the second was shifted far to the right of equilibrium (as written). The second reaction is primarily responsible for removing H atoms which are necessary to sustain combustion. As recognized by Day et al. [84], it is necessary to include recombination reactions such as

$$Br + Br + M \rightleftarrows Br_2 + M$$

to explain the observed flame suppression effectiveness of Br. Day et al. [84], suggests that the greater flame suppression efficiency of Br atoms as compared to Cl atoms results from the higher Br atom concentrations possible when H atoms and the hydrogen halide are in equilibrium.

Westbrook reported similar calculations for organic fuels in a series of three papers [85,86,87]. In the first paper, he considered the inhibition of methane and methanol-air flames by HBr [85]. Calculated flame behaviors were found to be in agreement with available experimental data. The inhibitor was predicted to be more effective for lean flames than stoichiometric or rich flames. Flame inhibition was primarily the result of the catalytic removal of H atoms via the mechanism discussed above.

In the second paper [86], the calculations were extended to include inhibition effects of HCl, HBr, HI, as well as, halogenated hydrocarbons formed by single substitution of Cl, Br, and I in methane, ethane, and ethylene. Preliminary findings for halon 1301, CF_3Br, were also discussed. The catalytic removal of H atoms was found to be the principal inhibition mechanism for each molecule. The only additional suppression reactions included beyond those for the hydrogen/air system discussed above were

$$H + RX \rightleftarrows HX + R$$

$$X + RX \rightleftarrows X_2 + R,$$

where RX is the halogenated hydrocarbon and X represents the halogen atom.

The calculations agreed with experimental observations in that compounds containing iodine were predicted to be slightly more effective inhibitors than their bromine analogs, while both were considerably more effective than the corresponding chlorine compounds. In the case of the halogenated hydrocarbons, variations in the fuel content of the parent species led to variations in inhibition efficiency with equivalence ratio. Effects of pressure changes were also characterized.

The final paper in the series by Westbrook [87] includes detailed numerical modeling results for CF_3Br-inhibited flames of hydrogen, methane, methanol, and ethylene. Good agreement between computed flame structures and the experimental determinations of Biordi et al. [75,76,77] was found. Flammability limits and burning velocities for the laminar flames were predicted and compared with experimental findings. The effects of variations in pressure, ambient temperature, and equivalence ratio were characterized.

The calculations described above must be considered as preliminary attempts to model fire suppression effectiveness. Our analysis has identified serious deficiencies with regard to some of the rate constants utilized in the calculations. On the other hand, these calculations are valuable because they indicate that flame modeling can provide important insights into flame suppression mechanisms. State-of-the-art calculations of this type are capable of modeling simple diffusion flames. Characterization of suppression behavior in flames of this type should be particularly illuminating.

e. Types of Diffusion Flames Used for Inhibition Investigations

Two types of configurations have been used to investigate the flame structure of inhibited diffusion flames. The first is the diffusion flame typical of a flowing fuel entering an ambient or coflowing oxidizing atmosphere. We will refer to this configuration as a "standard" diffusion flame. Normally these flames are stabilized at the mouth of the burner, and there is a region near the mouth where the flames are quenched. For certain fuels and burner configurations stable lifted flames can be created, while for other conditions blow out occurs. Note that it is possible to have some fuel and oxidizer mixing in the cool regions between the burner outlet and the flame base.

The second type is known as a counterflow diffusion flame. As the name implies, these flames are formed at positions where head-on flows of fuel and oxidizer meet. Two configurations are common. One involves flows moving in opposite directions. The second utilizes a porous cylinder placed in a flowing oxidizer (or less often, fuel) stream. Fuel (or sometimes oxidizer) is passed through the walls of the cylinder and a diffusion flame is stabilized around the cylinder. A stagnation point for the flow exists on the upstream side of the cylinder.

Since counterflow diffusion flames are located at positions removed from solid surfaces they are less subject to heat loss effects and premixing of fuel and oxidizer. For these reasons, measurements in counterflow diffusion flames tend to be more reproducible between different facilities. When the velocities of the fuel and/or oxidizer are increased, these diffusion flames are eventually quenched. This quenching occurs first at the flow-stagnation point in the center of the flame sheet. The flow velocity required to "open up" a diffusion flame provides a reproducible measure of diffusion flame extinction known as the flame strength.

f. Flame Chemistry and Structure of Inhibited Diffusion Flames

Most investigations of changes in flame structure due to the addition of an inhibitor have been made for standard diffusion flames. Several examples are discussed to provide insight into the types of measurements and understanding which have been achieved.

Simmons and Wolfhard [88] used spectroscopic techniques to investigate the flame structure of diffusion flames of ethane and carbon monoxide in air, both with and without, methyl bromide added to the fuel or oxidizer. A startling change in flame structure was found when the agent was added to the air. In the primary combustion zone emission intensities of continuum radiation (indicating increased soot concentration) and C_2 emission were observed as the inhibitor concentration was increased. Most unusual was the formation of a second reaction zone on the oxidizer side of the flame which showed considerable emission from excited bromine atoms. It was emphasized that reaction at this secondary location was not expected in the absence of the agent. Further tests demonstrated that this reaction zone was the result of the addition of the agent, which acted like a fuel. These results provided strong evidence that chemical reactions are responsible for flame inhibition.

Creitz [89] utilized gas chromatography to measure stable chemical species in the region outside of the flame zone for a propane diffusion flame. He observed that when CF_3Br was added to the oxidizer, the agent disappeared at positions outside of the flame where temperatures were too low for thermal decomposition. This observation is consistent with the observations of Simmons and Wolfhard [88] and suggests that chemical species generated by the flame interact with the agent.

Noda et al. [90] employed electron-spin resonance to measure the relative H atom concentrations within a methane Bunsen-type flame. Such a flame burns partly as a premixed flame and partly as a diffusion flame. The effects of adding a series of halogen-containing compounds on the H atom concentration were reported. For relatively low concentrations of the agents, H atom concentrations were decreased by amounts linearly related to the amount of agent added to the secondary air. The decreases were quite dramatic. For instance, the addition of 2 percent of methyl bromide to the air decreased the H atom concentration by 60 percent. The decreases in H atom concentrations were roughly correlated with inhibition efficiency with the amount of decrease increasing in the series $F < Cl < Br$.

Relatively few flame structure characterizations of counterflow diffusion flames are available. Ibiricu and Gaydon [91] reported spectroscopic results for ethylene-air and hydrogen-air flames to which inhibitors (methyl bromide, bromine, carbon tetrachloride, chlorine, or phosphorous oxychloride) were added. Their observations are similar to those of Simmons and Wolfhard [88]. They concluded that the inhibitors result in the removal of OH free radicals from the flames.

A method for stabilizing counterflow diffusion flames for liquid fuels was used by Kent and Williams [92] and Seshadri and Williams [93] to investigate flame structures for several organic fuels. Gases added to the oxidizer stream included N_2, CO_2, He, and CF_3Br. Some differences in the behavior of major species were found when these authors compared their findings to those of Creitz [89]. However, the rapid disappearance of CF_3Br as the flame zone is approached was observed in both types of diffusion flames.

Temperature measurements have also been reported for counterflow diffusion flames [92,93]. It was concluded that flame temperatures for conditions close to extinction are much higher when CF_3Br is added to the oxidizer than for nitrogen dilution. This is taken as support for a chemical mechanism for CF_3Br inhibition since N_2 is believed to inhibit flames only as the result of heat capacity effects.

g. Extinction of Laminar Diffusion Flames

The relative effectiveness of agents can be quantified by comparing the amounts which must be added to either the fuel or oxidizer in order to extinguish a diffusion flame. Both standard and counterflow diffusion flames have been widely used for such studies.

Early investigations involving standard diffusion flames are those of Simmons and Wolfhard [88] and Creitz [94]. Simmons and Wolfhard reported the percentages of methyl bromide which must be added to the fuel or air to extinguish flames of four organic fuels and hydrogen. In all cases the percentage of agent which had to be added to the fuel was much greater than required for the oxidizer. Extinction percentages were compared with measurements for premixed flames utilizing both the peak agent concentration and the percentage required for a stoichiometric mixture. The percentage of agent required for the oxidizer varied in similar ways as a function of fuel and, while larger for the diffusion flames, were of comparable magnitude to those necessary to prevent flame propagation in stoichiometric premixed flames. This is consistent with the view that the flame sheet in diffusion flames lies near positions of stoichiometric mixing.

Creitz reported similar measurements for a variety of fuels utilizing nitrogen, methyl bromide, and halon 1301 as inhibitors [94]. In this investigation, the concentration of oxygen in the surrounding atmosphere was also varied. As found by Simmons and Wolfhard [88], a considerably higher percentage of agent was required for extinction when added to the fuel than when added to the oxidizer. Creitz concluded that the mechanism of inhibition is different for the two cases. It is not clear whether he treated his data in terms of concentrations for stoichiometric combustion. One interesting conclusion was that for nitrogen/oxygen mixtures containing more than 25 percent oxygen, methyl bromide became a fuel and was entirely ineffective as a suppression agent. This compound burned as a diffusion flame in 32 percent oxygen.

Early measurements of percentages of inhibitor required to extinguish laminar diffusion flames were for gaseous fuels only. The results had a great deal of scatter for given fuel and inhibitor combinations [95,96]. This scatter was most likely due to variations between experimental apparatus and techniques. In response to this situation, Bajpai [96] developed an apparatus for determining the concentration of agents required to extinguish small pool fires of liquids. The device has come to be known as a "cup burner" after the shape of the vessel holding the liquid fuel. A coflow of oxidizer flows by the cup. In Bajpai's device the fuel surface had a diameter or 25.4 mm. Hirst and Booth have described a very similar apparatus having a cup diameter of 28 mm [97]. It is unclear if the flame will be strictly laminar for these conditions, but it is also true that the flame is unlikely to be fully turbulent. These devices will be discussed in greater detail because of their widespread use for testing suppression agents.

The percentage of agent required to extinguish a flame has been found to be a function of the oxidizer flow velocity, first increasing and then falling with increasing velocity [96,97]. Bajpai reported values of the peak percentages of halons 1301 and 1211 in air required to extinguish a wide variety of liquid fuels [96]. He found that his results agreed with the then-unpublished measurements made with a similar apparatus at Imperial Chemical Industries [97]. Hirst and Booth reported results for halons 2402, 1202, 1011, and 113 as well as halons 1301 and 1211. Bajpai [96] also compared his cup burner results with the findings of other researchers who measured percentages of agents required for extinguishment of much larger pool fires in enclosures [98,99,100]. Generally, peak percentages of agents for the two types of experiments were comparable, but values for the large-scale fires were smaller. Hirst and Booth made similar observations [97].

Sheinson and coworkers have reported peak percentages for a number of agents utilizing heptane and 2-propanol as fuels [45,46]. The results of these measurements are discussed in more detail in Section II-B-4-b.

Petrella and Sellers [101] had previously used a similar apparatus to investigate the extinction of propane diffusion flames. The gaseous fuel flowed from a round tube into the oxidizer coflow. Experimental results were reported in terms of the lowest oxygen index (LOI). This is simply the lowest oxygen concentration in air diluted with the agent which allows combustion to occur. Values of LOI were shown to be nearly independent of propane flow rate and to have only a mild dependence on the oxidizer flow rate. LOI values are reported for halons 1001, 1011, 1211, 1202, 1301, and 2402 as well as nitrogen. All of the brominated species gave LOI values of approximately 0.205 as compared to that for nitrogen of roughly 0.16.

Measurements have also been reported for percentage of agents in fuel or air required to extinguish opposed flow diffusion flames. One of the first investigations of this type is the study of Friedman and Levy [102]. These authors report the concentrations of various gaseous agents which must be added to the methane to open a hole in the flame sheet formed between counterflow jets of fuel and air. The effectiveness of various agents was ranked in the order $CH_3Cl < CCl_4 < CH_3Br < CF_3Br$, which is the same ordering reported by Rosser et al. [78] for the inhibition effects on flame speeds of premixed methane/oxidizer mixtures.

Milne et al. [103] used the counterflow geometry of Tsuji and Yamaoka [104] to investigate inhibition. In this configuration, fuel is supplied by a porous cylinder and the oxidizer flows by the cylinder. Extinction occurs at the stagnation point in front of the cylinder. Measurements are reported for agents added to both fuel and air for methane, propane and butane. Agents tested were CF_3Br, CF_2ClBr, CH_3Br, CO_2, Ar, and N_2. The ordering of agent effectiveness was consistent with measurements by other techniques.

Kent and Williams [92] and Sheshadri and Williams [93] report the amounts of CF_3Br and nitrogen in the oxidizer which are required to extinguish counterflow flames for liquid fuels.

h. Extinction of Turbulent Diffusion Flames

Tests of the ability of agents to extinguish turbulent diffusion flames are expected to most closely resemble the agents' use in the field to fight fires. At this point it is necessary to distinguish two common uses of halons: total flooding and local application. Total flooding is employed for firefighting in enclosures. The aim here is to create an environment in which the fire cannot exist by adding the agent to the entire atmosphere in the room at a concentration sufficient to inhibit combustion. Usually the enclosure is designed to be relatively airtight so that the agent concentration can be maintained above a specified level for several tens of minutes. Gaseous agents are employed for total flooding. Local application involves spraying the agent directly on, or near, the fire in order to induce extinguishment. Since liquids are more easily applied, agents used for this purpose are usually liquids which evaporate near room temperature or gases which condense just below room temperature.

Tests have been developed to assess agent effectiveness in both types of applications. These tests are usually less standardized than the tests previously described and utilize fire systems which are subject to a great deal of variability. As a consequence, these results show more variation so that reproducibility between different laboratories tends to be poor. Since they are the final step in the development of firefighting agents, many large-scale tests have been performed. Only a few are mentioned to provide a flavor of the types of studies which have been carried out.

Ford [2] discusses a number of large-scale fire tests which have been utilized to test the effectiveness of halon 1301. Results for both class A and class B fires are described. Three published examples of such tests were mentioned earlier [98,99,100]. The results of McKee et al. [105] and Alvares [106] for the extinguishment of pool and spray fire by halon 1301 and halon 1211 are also of interest. Investigations have shown that deep-seated smoldering fires in solid fuels often require considerably higher agent concentrations for extinguishment [28,107,108].

Fire tests involving direct application to fires in the open are less numerous. Ford [2] again provides a short review of previous tests. Malcolm describes some very early tests in which various halons were tested for their ability to extinguish Class B fires and cotton waste saturated with gasoline [6]. An editor's note in this paper (see Table XV, p. 128) points out many of the difficulties associated with this type of testing. Breen [109] has investigated the effectiveness of various mixtures of halons 1211 and 1301 for extinguishing heptane fires. A slight dependence of fire suppression efficiency on mixture fraction beyond a simple summation was identified. The author attributed this observation to differences in thermophysical properties between the two agents. Problems of reproducibility for this type of measurement are discussed.

The results of practical studies are usually published as internal reports and are sometimes difficult to access. An example of such work is a report which appeared as a Wright Air Development Division technical report [110]. Results for tests on a number of different size pool fires are discussed. Halons 1011, 1211, 2402, 1202, and 1301 were tested. Difficulties with reproducibility are discussed.

4. Agent Effectiveness, Testing Methods, and the Role of Different Suppression Mechanisms

a. Agent Effectiveness and Testing Methods

Many of the test methods which have been used to characterize the flame suppression capability of agents were discussed in the previous section. It is important to consider whether these tests are true predictors for fire suppression efficiency when the agents are utilized in real fire situations.

The effectiveness of an agent utilized as a total flooding agent is usually well correlated with its behavior in any of the several small-scale tests (e.g., explosion burette or cup burner). This is not surprising since cooling, dilution, and chemical flame suppression mechanisms (see the discussion in Sections II.B.2.a and .b) are expected to be most important in total flooding applications. In contrast, the performance of local application-agents does not correlate nearly as well with small-scale tests. This is due to the fact that these tests are insensitive to certain physical effects, such as evaporative cooling, smothering and mechanical blow off, which contribute to the effectiveness of streaming agents. Only test methods involving the direct application of these agents to fires (as liquids) will be able to account for these additional physical mechanisms.

b. Contributions of Physical and Chemical Mechanisms to Fire Suppression Effectiveness

Thus far, little mention has been made of the relative contributions of the various physical and chemical mechanisms to the flame suppression capability of an agent. This point is discussed here with reference to the published literature and the previous discussion.

As noted in the last section, very few of the tests used to characterize agents for fire suppression effectiveness screen for smothering or mechanical suppression. Perhaps as a result of this, the understanding of these processes remains very poor. No literature has been identified which attempts to quantify the contributions of these processes to flame suppression. The possibility of flame radiation blockage is even less well understood. These physical mechanisms will not be discussed further.

The majority of tests utilized for agent suppression efficiency characterization are expected to be sensitive to the physical processes of cooling and dilution and to any chemical mechanisms for flame suppression. Even for these mechanisms, the relative contributions of each to total agent suppression effectiveness are not well characterized.

Early studies focused on the role of inert agents in the extinction of flames. These studies are important since these gases are believed to play no chemical role in inhibiting combustion. As a result, their effectiveness can only be due to cooling and dilution. Therefore, these gases provide examples of flame suppression behavior where the mechanism can be characterized as well known.

Coward and Hartwell [111] reported on the extinction of methane flames by carbon dioxide, nitrogen, helium, and argon. These workers showed that the "extinctive action" of CO_2, Ar, and N_2 were nearly in the inverse ratio of their heat capacities and concluded that heat removal from the reaction zone was the principal mechanism of flame inhibition. Helium was found to be more effective than predicted, based on heat capacity effects alone. This was attributed to the high thermal conductivity of this low molecular weight gas and suggests that thermal heat transfer plays a minor, but detectable, role in an agent's effectiveness.

In 1925 White [112] suggested that flame temperatures for a given fuel-air mixture were nearly constant at the lower flammability limit and were independent of the initial temperature of the mixture. The limiting temperature did vary from fuel to fuel. An experimental investigation by Simmons and Wolfhard [113] for a number of fuel-air mixtures diluted by nitrogen supports this conclusion. Many authors have applied the idea of a well-defined limit temperature to the understanding of the effects of inert gases on the flammability limits of fuel-oxidizer mixtures.

Egerton and Powling [114] calculated adiabatic flame temperatures for hydrogen and methane flames at their lower flammability limits when the nitrogen in air was replaced with CO_2, Ar, and He. With the exception of added helium, the calculated flame temperatures were roughly the same. The limiting temperature with helium was higher which is consistent with the findings of Coward and Hartwell [111] concerning the importance of the high thermal diffusivity of this light gas.

Flame temperatures for methane flames at their fuel and oxidizer extinction limits were measured by Ishizuka and Tsuji [115] in a counterflow diffusion flame. The oxidizer used for the experiments was oxygen mixed with N_2, Ar, or He. For N_2 and Ar, the flame temperatures were very close (± 30 K) to 1500 K. In the cases where the oxidizer contained helium, flame temperatures were roughly 1640 K. The slightly higher temperatures which were observed for helium mixtures are consistent with previous conclusions concerning the limited role thermal conductivity plays in the determination of extinction limits.

Ewing et al. [116] have also considered the effects of inert diluents on temperatures at flame limits. They calculated adiabatic flame temperatures and concluded that the limit temperatures were functions of the molecular weight of the inert extinguishants. Both diffusion flames of heptane in air and premixed flames of methane/air were considered. An explanation was not provided as to why the limit flame temperature behavior they find differs from that reported by other authors.

There is widespread agreement that the fire suppression effectiveness of certain agents is beyond what would be expected on the basis of their ability to extract heat. Much of the literature discussed in Section II.B is based on the hypothesis that chemical mechanisms are active. Fryburg [55] provides a good review of the justifications for a chemical mechanism based on work published prior to 1950. The following paragraph quoted from this work is typical of the literature.

"The importance of the chemical actions are indicated by the greatly enhanced extinguishing effectiveness of the gaseous and liquid halogen-containing compounds, as determined in inflammable-limits studies. These compounds have larger specific heats than the inert gases and the cooling action would therefore be increased, but the increase is not large enough to account for the much greater effectiveness of many of the compounds investigated by Jorissen." (See references [117,118,119].) "In addition, there is no relationship between extinguishing effectiveness and specific heat among the halogen compounds. This effect therefore must be derived from strong chemical actions."

Additional evidence for a chemical mechanism of flame suppression is available in results for the effect of suppressants on the flame temperature at limit concentrations. It has been shown earlier that physical suppression does not change limit temperatures significantly. Burdon et al. [74] investigated the effect of methyl bromide on H_2-air and CO-air flames. As part of the investigation adiabatic flame temperatures were calculated for limit mixtures. These limit temperatures were found to increase substantially as the methyl bromide concentration was raised and the authors concluded that the temperature rise "may be attributed to the chemical intervention of methyl bromide in the flame reactions" [74].

Simmons and Wolfhard [88] reached an identical conclusion based on measurements on methane-air mixtures inhibited with bromine and methyl bromide. Simmons and Wright [120] considered the system of propane-air-hydrogen bromide. Adiabatic flame temperatures increased from 1590 K at the lean limit with no hydrogen bromide to 2100 K for a mixture containing a concentration of HBr which was just short of the peak percentage.

As part of a study which argues that extinction of hydrocarbon flames can be understood based solely on heat-absorption processes (even for the "chemical" suppressants), Ewing et al. [116] found that for certain classes of suppressants the calculated limit flame temperature was raised considerably above that observed for inert suppressants. Even though it is not the aim of the authors, this observation provides additional support for a chemical mechanism.

Section II.A.4.d noted that, for flames in which only heat loss mechanisms are important, roughly 210 J/K per mole of O_2 are required to suppress a flame. Tucker et al. [47] used this idea to analyze the effects of inert diluents and halon 1301 on various fuel-oxidizer combinations. Based on the nitrogen results, predictions were made for the heat capacity contributions required from CO_2, He, and CF_3Br. The experimental amount of CO_2 was predicted within 10 percent, but the amounts of He and CF_3Br required were greatly overpredicted. We have seen previously that helium gas results in higher heat losses from the combustion zone due to its unusually high thermal conductivity and therefore more easily extinguishes flames than heavier molecules. Tucker et al. [47] concluded that the overprediction of the amount of CF_3Br required is due to a chemical effect of this halon on the flame chemistry.

Using a cup burner test with n-heptane as the fuel Sheinson et al. [45,46] have determined the amounts of various agents required for extinguishment. They have analyzed their results in terms of the heat capacity of the flame gases per mole of oxygen. Inert agents are found to require roughly 210 J/K for extinguishment. Certain agents such as CF_3Br and CF_3I require considerably less heat capacity for the gas mixture. This decrease in the required heat capacity is attributed to a chemical mechanism for flame suppression.

As we have seen, chemical mechanisms of flame suppression have been hypothesized and tested for many decades. Despite this, until recently there have been no attempts to quantify the relative contributions of physical and chemical mechanisms to the flame extinguishment process. The first attempts, of which we are aware, are those of Larsen [121,122,123] and Ewing et al. [116]. These authors reached the somewhat startling conclusion that flame suppression is the result solely of a physical mechanism. This was argued to be true even for the so-called chemical suppressants.

In the earliest of these papers [121] Larsen found that the effectiveness of halogen atoms for fire suppression was directly proportional to their atomic weights. It was argued that this supported a physical mechanism for their extinguishment capabilities, but no hypothesis was made as to why fire suppression effectiveness should scale with atomic weight. It is very likely that some other physical property which scales with atomic weight (e.g., hydrogen halide bond energies decrease with increasing halogen molecular weight) is the source of the observed correlation.

In another paper [122], it was demonstrated that the flame suppression capabilities of inert agents could be understood in terms of heat capacity effects. Larsen argued that a similar analysis of peak concentration data for a number of halons suggested that the effectiveness of these agents was also due to exclusively heat capacity [123]. Instead of calculating the total heat capacity of the gases at the flame limit, Larsen reported values for three ratios (K_{IO}, K_{IF}, KC_p) of heat capacities. K_{IO} is the ratio of the heat capacity of the agent to the total heat capacity of a mixture of oxygen and inert which is chosen such that, when the fuel is added, the mixture passes through the peak concentration. K_{IF} is a similar ratio for a fuel-agent mixture. KC_p is the ratio of the total heat capacities of the inerts and the total heat capacity for all gases. All heat capacities are for a temperature of 298 K. Values of K_{IO} and K_{IF} were found to be roughly constant. Larsen argued that this observation supports his contention that only heat capacity effects are important for flame suppression effectiveness.

The monograph [123] where Larsen's paper appeared includes comments from the participants of the conference [124]. Many of them questioned the analysis and conclusions which Larsen reached. Perhaps the most important critique was offered by J. W. Dehn. In his comment, Dehn noted that the ratios of heat capacities employed were determined primarily by the heat capacities of nitrogen and air. Variations in other additives would have minor effects on their values. Consequently, these ratios would not be expected to be very sensitive indicators of fire suppression efficiency.

Sheinson et al. [45,46] and Ewing et al. [116] have performed analyses based on the total heat extraction capabilities of combustion product gases which seem to be more realistic than those employed by Larsen [122,123]. Sheinson et al. calculated the heat capacities available per mole of O_2 for n-heptane diffusion flames burning at their limit in air/agent mixtures. Seven agents which are expected to be inert in the flame gave values covering a range of 180-205 J/K(mole-O_2). The lowest value was for helium which is expected to have a lower value due to its high thermal conductivity. Values for agents which are expected to take part in the chemistry of the flame (CF_3Br and SF_5Br) required only on the order of 155 J/K(mole-O_2). This is taken as strong evidence for a chemical mechanism of flame suppression [45,46].

A different type of analysis was provided by Ewing et al. [116]. These authors calculated the heat extraction behaviors for a number of fuel/air combustion systems in the presence of various agents (including solids) and made the assumption that extinction occurs for well-defined flame temperatures. In this way they were able to correlate the findings for a wide variety of suppressants added to flames. As discussed above, inert species gave limit temperatures which varied little and are relatively low. This behavior was not observed for those agents which are traditionally considered to be chemically active [116]. The total heat extraction capability of these agents was too low to be the sole source of extinction. Note that this conclusion is at variance with Larsen's [123] contention that only heat capacity effects need be considered. Ewing et al. noted that agents such as CF_3Br can absorb additional heat by decomposing. Even though decomposition is a chemical process, this is classified as physical extinction since there is no direct interaction with the combustion chemistry (this viewpoint is consistent with that discussed in Section II.B.2.c). Better agreement was obtained when these additional heat extraction mechanisms were taken into account. The major conclusion of this work was that "for most substances the extinguishing capacity is related to heat-extraction and that many of the effects previously attributed to chemical mechanisms may be thermodynamic in nature rather than kinetic."

Interestingly, these authors had to assume that the limit temperature varied for different types of agents [116]. For agents which in the past have been classed as chemically active, including some solids, the limit temperatures were considerably higher than for inert gaseous species. As discussed above, such changes in the limit temperature can be taken as evidence for a chemical mechanism. This work is important because it emphasizes that all mechanisms for heat removal must be considered in assessing the physical effects of an agent. Furthermore, it provides a prescription for accomplishing this. On the other hand, the conclusion that only physical processes are responsible for extinguishment is not consistent with the increases in limit temperatures which are required in order to obtain correlations of flame suppression effectiveness for different chemical families.

Sheinson et al. [46,125] incorporated some of the ideas of Ewing et al. [116] into a model which attempts to quantify the roles of physical and chemical mechanisms on agent effectiveness. Their model assumes that physical and chemical effects are additive. Physical contributions are determined by calculating the heat which can be extracted from the flame by the heat capacity and chemical decomposition of the agent. As discussed above, a total of roughly 210 J/K(mole-O_2) are required to inert a mixture.

Cup burner measurements of extinguishing agent concentrations for an n-heptane pool fire were used for the analysis by Sheinson et al. If the mixtures required less than 210 J/K(moles-O_2) the difference was attributed to chemical suppression effects. The assumption of a linear relationship allowed the relative fractions of physical and chemical suppression to be reported. Interestingly, two agents tested, SF_5Cl and S_2F_{10}, seemed to enhance the fire. In agreement with past investigations, it was concluded that CF_3Cl, CF_3Br, CF_3I, and SF_5Br act as chemical flame suppressants. As an example, these authors conclude that the suppressant effects of CF_3Br are 20 percent physical and 80 percent chemical [46,125].

The analysis of Sheinson et al. [46,125] is recent, and considerably more development and testing are required. However, the work does provide the first steps toward quantifying the contributions of physical and chemical mechanisms to flame suppression. If ideas of this type can be further developed, it may become possible to tailor molecules to maximize physical and chemical contributions to flame suppression behavior.

c. Conclusions Regarding a Chemical Mechanism for Fire Suppression

There is widespread agreement that combustion reactions can be interrupted by the application of certain fire suppression agents. Most researchers conclude that interference with the flame chemistry increases the effectiveness of such agents significantly as compared to that expected based on heat extraction effects alone. The modern understanding of combustion chemistry and kinetics identifies the most likely chemical mechanism for fire suppression as an interruption of the important free radical chain reactions responsible for maintaining the high heat release rate. The most likely species for attack by a chemical agent or its products is the H atom.

The fact that some uncertainty remains concerning the chemical mechanism of flame suppression can be traced to the relatively poor characterization of the process. Recent attempts have been made to quantify the relative contributions of physical and chemical mechanisms to the effectiveness of fire suppression agents. The tools available to modern combustion scientists should allow these uncertainties to be resolved in the near future.

Based on the extensive literature review discussed above, we have concluded that chemical fire suppression does occur and that chemical mechanisms contribute significantly to the fire suppression capabilities of many agents. For this reason, the ability to develop principles of chemical fire suppression has played a major role in selecting compounds for the exploratory list.

C. HALON STABILITY AND DEPLETION OF STRATOSPHERIC OZONE

1. Stability and Properties of Halons

As discussed above, the current commercial halons used for fire suppression have many desirable properties. In almost every case, these favorable properties can be traced to the unusual chemical stability of these molecules. In many systems, including the atmosphere and living organisms, the species most likely to be responsible for chemical attack on a given molecule is the highly reactive hydroxyl free radical, OH. Due to the relative strength of carbon-halogen bonds compared to the relatively low bond energies of possible products, OH reactions with fully halogenated species are slow. In contrast, for molecules containing carbon-hydrogen bonds, OH free radicals can abstract the hydrogen atom rapidly to create a new carbon-based free radical and a water molecule. The resulting free radical reacts rapidly with O_2 and is ultimately destroyed.

The lack of significant reactions and the low polarity of the current commercial halons mean these molecules are nonconducting and thus safe for use on electrical equipment. The nonreactivity of the molecules is the principal reason why the species have low toxicity. The normal processes which cause toxic responses in organisms do not take place. The low reactivity of totally halogenated species also means that they do not react easily with other materials and, therefore, have good compatibility properties.

In combustion, molecules can be destroyed by unimolecular decomposition or attack by H and OH radicals. Commercial halons such as CF_3Br (halon 1301) are unreactive towards OH. They tend to be about as reactive towards H atoms as are more typical fuel molecules (via $H + CF_3Br \rightarrow CF_3 + HBr$), but are more likely to undergo unimolecular decomposition (to $CF_3 + Br$). These reactions release Br and HBr which are thought to play important roles in the mechanism of chemical fire suppression. The subsidiary question, which will be addressed in the course of testing the candidate compounds, is whether the details of the mechanism and the rate of halogen release affect fire suppression activity. This can be addressed through experimental work coupled with chemical kinetic modeling. It may well be that there is only a narrow "window" for effective chemical suppressant activity. If this can be established, it will open the way to designing molecules for specific fire suppression situations.

2. Brief Introduction to Atmospheric Structure and Chemistry

The earth's atmosphere is a dynamic and complicated physical system. In this section, we introduce some very simple descriptions of the structure and chemistry of two regions of the atmosphere, the troposphere and the stratosphere, to provide a background for the following discussion on depletion of stratospheric ozone by the current commercial halons. Details can be found in a number of textbooks (e.g., [126,127]). A report describing the outcome of the Alternative Fluorocarbon Environmental Acceptability Study (AFEAS) [128] is also relevant. It contains an excellent discussion of these topics including an examination of compounds designed to replace the widely-employed chlorofluorocarbons (a subclass of halons). Dr. John Herron discusses many of the concepts of atmospheric chemistry related to the current commercial halons in the companion report "Preliminary Screening Procedures and Criteria for Replacements for halons 1211 and 1301 [129]."

The troposphere is the region of the atmosphere extending from the earth's surface to a height denoted as the tropopause. The tropopause separates the troposphere and the stratosphere. The height of the tropopause varies with location and season, but is on the order of 11 km [126]. The stratosphere lies above the tropopause and extends to a height of roughly 50 km where the stratopause is located. The next region of the atmosphere is known as the mesosphere.

The troposphere is a region of rapid air movements and intense mixing. As a result, it is reasonably uniform; and chemical species released here are dispersed and mixed within the layer quite rapidly (on the order of a few weeks). Air pollution in urban areas is the result of chemical processes occurring in this region of the atmosphere. The chemistry is very complex [127] and no attempt is made here to discuss it. It is worthwhile to reiterate that hydroxyl free radicals are by far the most important species responsible for chemical attack in the troposphere.

There are a number of processes by which a molecule can be removed from the troposphere:

- Reactive molecules undergo chemical transformation in the troposphere and in most cases eventual removal from the atmosphere.
- The troposphere is subject to sunlight having wavelengths greater than 290 nm. If a molecule absorbs at these wavelengths, it is possible that photolysis may occur. Photolysis creates reactive species and eventually leads to the removal of the molecule from the troposphere.
- If the molecule is water-soluble or capable of hydrolysis, it can interact with moisture in the troposphere and eventually "rain out."
- If the molecule survives long enough it can eventually diffuse into the stratosphere.

Temperatures generally fall with height in the troposphere. This trend is reversed in the stratosphere where temperatures begin to increase with altitude. This temperature rise occurs as the result of absorption of the sun's radiant energy at wavelengths shorter than 300 nm by ozone, O_3 [126]. As a result of the change in temperature behavior with height, mixing across the tropopause is very slow. Chemical species released in the troposphere require several years to diffuse into the stratosphere.

Ozone is formed in the stratosphere as the result of photolysis of oxygen by sunlight to create oxygen atoms followed by recombination of the atoms with oxygen molecules to form ozone. These reaction processes can be written as:

$$O_2 + h\nu \rightarrow 2O$$

$$O + O_2 + M \rightarrow O_3 + M,$$

where $h\nu$ represents a photon having a wavelength shorter than 220 nm and M is a third body required to remove excess thermal energy.

There are also chemical processes taking place in the stratosphere which remove ozone molecules. The equilibrium concentration of ozone in the stratosphere is the result of a balance between these destruction and formation processes. O_3 is found throughout the stratosphere with a maximum concentration at a height of approximately 25 km.

3. Current Commercial Halons and Depletion of Stratospheric Ozone

In section I.B.1.b it was pointed out that the current commercial halons are generally recognized as contributing to the depletion of ozone in the stratosphere. It is now possible to discuss the reasons for this conclusion in more detail.

Current commercial halons have been, and continue to be, released into the atmosphere by a variety of mechanisms. These include discharges during firefighting, training, testing of total flooding systems (efforts are underway to limit this activity), and leaks [7]. In the vast majority of cases these releases take place in the troposphere. The current commercial halons have very long tropospheric lifetimes due to their unusual chemical stability. As a result, they eventually diffuse to the stratosphere. As the molecules rise in the stratosphere they are exposed to shorter wavelength light. Eventually, a height is reached where the current commercial halons begin to absorb this higher energy light and undergo photolysis which releases bromine atoms. The bromine atoms are highly reactive and initiate a catalytic chain reaction which converts ozone to oxygen molecules in the following manner:

$$\begin{array}{ll} & Br + O_3 \rightarrow BrO + O_2 \\ & \underline{BrO + O \rightarrow Br + O_2} \\ \textbf{Net:} & O_3 + O \rightarrow 2O_2. \end{array}$$

As a consequence of this mechanism, the rate of destruction of ozone is increased. This leads to a reduction of the equilibrium concentration of ozone in the stratosphere. Once introduced into the stratosphere, bromine atoms have very long lifetimes; and the destruction of ozone can continue for decades. Chlorine and iodine atoms also catalytically destroy ozone in the stratosphere. Fluorine atoms are recognized as being relatively unimportant, since effective mechanisms are available for chain termination.

A widely used concept to characterize the ability of a specific type of molecule to catalytically destroy ozone is the ozone depletion potential (ODP). Several parameters must be considered in deriving this number. These include: tropospheric lifetime, diffusion time from the troposphere to the stratosphere, effectiveness in destroying ozone, and possible sinks (removal processes) for the reactive species created from the molecule in the stratosphere. Such calculations are subject to a great degree of uncertainty and are thus difficult to quantify. As a consequence, values are usually reported relative to the results for CFC-11, CCl_3F, as first suggested by Wuebbles [130]. This ratio has come to be known as the ODP value. As noted above, ODP values for two of the current commercial halons are estimated to be 2.7 (halon 1211) and 11.4 (halon 1301).

As discussed in Section I.B.1.b reductions of stratospheric ozone have been observed which are attributed to the release of manmade halons (both current commercial halons and CFCs) into the stratosphere. The production of these chemicals has been limited by the Montreal Protocol. It is ironic that the chemical stability of the current commercial halons, which makes them so useful for fire suppression, is responsible for their ability to destroy stratospheric ozone, and will ultimately limit their use.

4. Means for Reducing ODP Values of Effective Firefighting Agents

The use of current commercial halons will be strictly limited or curtailed entirely in the future. The challenge is to find replacements which are effective and safe as fire suppression agents and which are less harmful to stratospheric ozone than the current commercial halons. In this section possible means for identifying fire suppression agents which are safe for stratospheric ozone are discussed.

The present understanding suggests that there are two general mechanisms for limiting the destruction of stratospheric ozone by molecules which are effective as fire suppressants. The first is to employ agents which contain no chlorine, bromine, or iodine. This requires that agents which are recognized as being the most effective fire suppression agents, including the current commercial halons, cannot be employed. The second approach is to use agents which are destroyed over short time scales within the troposphere and thus do not have time to diffuse to the stratosphere.

For the first approach it is necessary to utilize only perfluorinated organics or other classes of molecules which do not contain Cl, Br, or I. This approach severely limits the number of possible agents and removes large classes of molecules which have been shown to be effective fire suppression agents.

The second approach, employing molecules which are effectively destroyed in the troposphere, might allow some molecules containing the heavier halogens to be used. The discussion in Section II.C.2 provides insights as to how halons might be destroyed in the troposphere. These destruction mechanisms will be discussed by considering the possibility of modifying one of the current commercial halons to dramatically reduce its lifetime in the troposphere. Keep in mind that the discussion is general, and similar considerations will apply to the entire halon family.

Possible modifications to current commercial halons for reducing tropospheric lifetimes include:

- providing a site for OH free radical attack,
- extending the absorption region of the molecule toward the red so that solar wavelengths reaching the troposphere can photolyze the molecule, and
- increasing the solubility or susceptibility to hydrolysis so that the molecule will rain out of the atmosphere.

As examples of these concepts, consider some possible molecular modifications for halon 1301. Keep in mind that these modifications are provided only to demonstrate principles. No claim is made that these particular molecules will be appropriate alternatives for halon 1301. The susceptibility of halon 1301 to chemical attack by OH can be increased by substituting an H atom for one of the fluorines to give CF_2HBr (halon 1201). The lifetime of this molecule in the troposphere will be reduced compared to that for CF_3Br. A second approach is to red-shift the absorption spectrum of the CF_3Br. One means of doing this is to replace the bromine atom with iodine-yielding CF_3I (halon 1301). CF_3I should be an effective fire suppression agent. Its absorption spectrum is red-shifted from that for CF_3Br which should increase the probability that it will photolyze in the troposphere. Since the solubility of a molecule in water and its susceptibility to hydrolysis both increase with molecular polarity, it is possible that tropospheric lifetimes might be decreased by increasing the polarity of CF_3Br. For example, halon 1201 is more polar than halon 1301 and would, therefore, be expected to have a shorter tropospheric lifetime.

Modifications discussed here are designed to increase the reactivity of the molecular species. Such changes are also likely to result in variations in physical properties and characteristics (e.g., fire suppression effectiveness, toxicity, and materials compatibility) which make the molecule less likely to be useful as a fire suppressant. It is certain that a careful balancing of properties will be required to provide an effective and safe fire suppression agent which is also less harmful to stratospheric-ozone than current commercial halons. This is the primary challenge to the fire protection community.

SECTION III

FAMILIES AND COMPOUNDS INCLUDED ON THE LIST

A. INTRODUCTION

This section describes the development of the list of compounds. The discussion is broken down into a series of chemical families. A discussion is provided as to why these families were chosen, as well as, a summary of previous measurements of fire suppression effectiveness for representative compounds from each family. The subsections conclude with a tabulation of the names and relevant properties for the family members which are included in the final list.

B. SATURATED HALOCARBONS

1. Justification for Consideration

The saturated halocarbons or halons ($C_nF_oCl_pBr_qI_r$ where $o+p+q+r=2n+2$) are well established as flame suppressants [66]. Halons containing iodine are treated as a special case and are discussed later. Their mechanism for suppression is not fully resolved between two proposals:

- first, chemical action via catalytic recombination of chain carriers [55]; and
- second, physical action via increasing the capacity of the system to absorb heat [121,122,123].

In either case, a large number of halocarbons exist that would provide the necessary recombination agent (Cl or Br) or adequate stability and heat capacity. The appeal of the current commercial halons was primarily their relative safety and lack of residue. The safety allowed compounds such as halons 1301, 2402, and 1211 to be used without the need for alternative life support systems in a large number of environments. The lack of residue and the nonionic character of the compounds also made them ideal for dealing with fires in sensitive electrical equipment. All of these compounds are very stable to reaction, and this very stability makes them such a threat to the ozone layer. The halons used in fire suppression are not destroyed in the troposphere, but are reactive in the stratosphere. In addition, all of the species listed above contain bromine, which has proven to be much more destructive to the ozone on a per mole basis than chlorine.

The strategy for dealing with the relatively high ozone depletion potentials of the current commercial halons is to provide alternative compounds that either do not reach the stratosphere or, if reaching the stratosphere, do not participate in catalytic destruction of ozone. In the case of the CFCs (a subclass of halons) used in refrigeration and for solvent applications, this has meant a fairly simple modification - adding a hydrogen to the molecule. The resulting molecule will be destroyed in the troposphere in a time that is short relative to its tropospheric residence time by reactions with atmospheric hydroxyl radicals. It is also possible to design molecules that will react in sunlight and be destroyed in the troposphere. Finally, within the halocarbons we may seek molecules that do not destroy stratospheric ozone.

The difficulty in designing such molecules does not come from the requirement that it put out a fire, or even from the requirement that it not destroy ozone, but rather from the requirement that these compounds have low toxicity. To see this, one need simply to look at the effects of addition of H atoms to any brominated compound. As an example we can use halon 2402, CF_2BrCF_2Br, which can be hydrogenated in a number of ways. The simplest for this discussion would produce CF_2HCF_2Br. This molecule would be expected to react reasonably rapidly in the atmosphere, since the H atom is available for reaction with OH. At the same time, it may be expected to undergo hydrolysis in an ionic medium to produce HBr and C_2F_4 more rapidly, and, since it would be expected to have a larger dipole moment, to be more soluble in an ionic medium. Hydrolysis in rain droplets would be faster and thus aid in the destruction of the compound; but solubility in blood and subsequent reaction could make the compound more toxic.

Even in cases where the halon is not acutely toxic, it may have side effects that must be considered. For example, one of the compounds listed below as a candidate, halothane ($BrClHCCF_3$), is an anesthetic. Halothane has been in clinical use for over 30 years so there is a substantial body of data on its side effects [131]. It is not especially toxic, but there is evidence, as there is for other halocarbons, that cardiac sensitization does occur. In addition, the very fact that the compound is an anesthetic makes it necessary to exercise caution in using it as a general replacement for the current commercial halons. While these precautionary comments must be noted, it is also true that, with regard to toxicity, very small changes in the structure of the compound can greatly change the physiological effect [132]. The compounds suggested should be viewed as a starting point for further work and not as a final list. As studies on the toxicity and the fire suppression effectiveness of these compounds are extended, new, closely related compounds may well suggest themselves for study.

In producing a list of compounds, two basic criteria were applied:

- the compound should have some feature that suggests it would not be as destructive to the ozone layer as the current commercial halons,

- it should test the basic ideas as to how halocarbons affect flames.

In addition, wherever possible, compounds with low toxicity were sought. In many cases, however, the toxicity data was not available.

The result of applying the first criterion was that only compounds containing a hydrogen atom, compounds containing no chlorine or bromine, or compounds that might be photoactive were included. The first alterative has been discussed briefly above. It simply states that if there is an H atom in the molecule, the rate of reaction with atmospheric OH might be fast enough to destroy the molecule in the troposphere before it reaches the stratosphere. The second alternative requires that the molecule be fully fluorinated. (Iodine-containing halons are discussed separately in Section III.F.) The final alternative can be stated as requiring either that the molecule have more than one Br/Cl on a single carbon, or that there be some other feature in the molecule that shifts the absorption cross section toward the red enough that the solar radiation flux in the troposphere would be sufficient to photolyze the molecule in a time short compared to the time expected for the molecule to reach the stratosphere.

The second alternative--the fully fluorinated compounds--is the simplest to discuss and so we shall begin with it. There has been extensive work on the use of perfluoroalkanes as fire suppressants, partly as a result of the desire to create atmospheres that would sustain life and not combustion [44,48,133]. In addition, the fluorinated analog of cyclobutane has been suggested as a possible fire suppressant. The inclusion of these compounds has the further benefit of testing one of the two proposed mechanisms of fire suppression and thus satisfies the second criterion for selection. The perfluorinated compounds are less reactive than other halocarbons. It is generally assumed that CF_4 is inert and thus differences between it and C_1 (single carbon) halocarbons containing Br or Cl may be analyzed in terms of the difference between the chemical and physical effects. The larger perfluorinated compounds are less reactive than the corresponding bromine-substituted compounds, but since the C-C bonds are about the same strength as those of hydrocarbons they are not totally inert in a flame.

The third alternative--photoactive compounds--requires data that are difficult to measure. The solar flux in the troposphere starts to increase dramatically at exactly the point that most of the current fire suppressants have steep decreases in their photoabsorption cross sections [134,135]. However, by putting two bromines or a bromine and a chlorine on the same atom, the absorption cross section shifts toward the red and the resulting tropospheric lifetime is decreased. In addition, the cross section will shift toward the red if the molecule is made larger. Going from C1-C2-C3 provides a steady, but small shift toward the red [136]. Data for most molecules is difficult to find in the literature, and because the absorption cross sections are small, the measurements are subject to impurity effects.

The first alternative - adding H to the halocarbon - is essentially that being followed by the research leading to alterative refrigerants and solvents. For these compounds, all hydrogenated chlorofluorocarbons, the problem of hydrolysis, discussed above, is much less acute because of the increased C-X bond strength of Cl/F compounds relative to Br compounds. Thus one mode of toxicity is reduced. Beyond the toxicity effects there are also the effects on the physical properties of the molecule. In general, if one of the fluorines is replaced with a hydrogen, the boiling point of the compound will increase due to increased polarity. This is slightly offset by the decrease in boiling point due to decreased molecular weight, but, in general, the boiling point will increase upon H substitution. Replacing chlorine by hydrogen generally results in a decrease in boiling point. Most other physical properties show similar predictable variations with substitution. The hydrogen-substituted compounds also offer the greatest scope for examining some of the proposals for understanding fire suppression.

The idea of endothermicity affecting fire suppression is at the heart of the argument that fire suppressants work by adding to the heat loss mechanisms in the fire. While the suggestion that endothermic processes are important is not new [116], it has not been systematically explored. In a theoretical calculation one could increase the heat capacity of an additive species indefinitely and at some point the fire would no longer propagate. Curiously, this has not been done within the context of modern flame modeling calculations. In practice, the larger the molecule, the greater its heat capacity. There are, however, other ways of increasing the heat-absorbing potential of a molecule. One of these is to find molecules that undergo endothermic reactions to produce stable products. A simple example of this sort of process would use a hydrogen-substituted analog of halon 2402. In this case, like the example earlier, one of the bromines would be replaced with an H atom, resulting in CF_2HCF_2Br. This molecule could eliminate HBr to form $CF_2=CF_2$ [137] in a reaction that was estimated by functional group contributions to be about 138 kJ/mole endothermic. The reaction rate has not been measured, but can be estimated to occur readily in a temperature range of 300-800°C. The 138 kJ/mole exothermicity is converted to a heat absorbed per gram, it corresponds to about 760 J/g. This should be compared to a total heat absorbed by halon 1301 in going from room temperature to 500°C of about 230 J/g. The reaction endothermicity is in addition to the heat capacity of the starting material, which would be expected to be larger than that of halon 1301. Even if only 20 percent of the halon underwent this reaction, it would still represent an addition of 150 J/g to the heat extraction capability of the system.

There are other important endothermic pathways; one is simple bond breaking. The C-Br bond strength in CF_3-Br is 290 kJ/mole, but the rate constant for bond dissociation is too small for this process to have an effect at temperatures below about 700°C [138]. If the bond energy were lower by about 40 kJ/mol, there might be substantial effects from bond breaking processes of this type. There has been very little exploration of this class of reactions as an explanation of fire suppression effectiveness.

2. Past Flame-Suppression Measurements

The literature on halogenated hydrocarbons is extensive (see Section II.B). A note of caution must be included in any survey of fire test results. First, the results are often indicative, not predictive: small changes in the test configuration will change the results dramatically. Second, there are two approaches that are often in conflict: the "full-scale test" and the "research project." An experiment using a premixed flame and suppressant added to the fuel gas before combustion is likely to yield different results than an experiment with a diffusion flame with the suppressant added in the oxidizer stream. Both of these would probably be classed as "research projects" and might correspond to the results of spraying a suppressant agent at a fully turbulent pool fire. Each of these experiments has value, and all need to be done. However, the interpretation of the results for each kind of experiment relative to another must be made with extraordinary care. The role of chemical and heat-capacity effects is best determined with the more controlled research scale tests, but the final choice as to which of otherwise equally effective agents should be used must be made with a clear understanding of how the material will be used in practical applications. In general, when trying to assess data, it is best to find a single experiment done on a large number of compounds--even if the experiment is not ideal.

The earliest, and, in many ways, the most complete, of the tests of fire suppression agents is the Purdue Foundation Study [25]. In this study over 50 compounds were tested. In the most extensive set of tests, the compounds were added to n-heptane/air mixtures and the amount of the test compound required to suppress combustion for all heptane/air mixture ratios was reported. The data were taken under reduced pressure conditions - typically 0.4 - 0.8 atm, and generally over a range of stoichiometric conditions (1-6 percent heptane, corresponding to stoichiometric ratios of 0.5 to 6 in the absence of inhibitor). Not every inhibitor had the full range of coverage (2-5 percent was the most common), and in most cases only about 16-20 separate experiments were preformed.

There is no comparable body of data on diffusion flames, or oxygen index type tests. For these tests, one would use a diffusion flame and add suppressant to the oxidizer stream. The results from such a test more nearly simulate the effects of a total flooding system. In broad outline, the results would be expected to be similar, but not identical, to the results of the flame propagation experiments from the Purdue Study. Very few experiments have been done along these lines, although the work of Creitz [89,94] examined not only the effect of agent addition to the fuel and oxidizer, but also the effect of different fuels. Unfortunately, only two inhibitors were investigated. Simmons and Wolfhard [88] did similar experiments in a different burner configuration. (The cup burner test series discussed above studied a diversity of fuels, but focussed on halons 1211 and 1301.)

3. Recommendations

The saturated halocarbons chosen for inclusion on the list will be subject to revision. Small changes in the structure - moving a hydrogen from the end to an interior carbon, replacing a bromine with a chlorine, switching the position of a fluorine and a bromine - can have very large effects on toxicity, with possibly only minor effects on the fire suppression effectiveness. The recommendations are broken up into three groups based on the rationale for believing the molecule will not deplete the ozone layer. The first group is selected because they have no chlorine or bromine in the molecule. The chemicals in the second are probably photoactive and are more likely to be destroyed by sunlight in the troposphere. In the third group, all the chemicals contain hydrogen.

a. Perfluoro Compounds

The fluorinated analogues of methane, ethane, propane, n-butane and cyclobutane are initially considered. In addition, it may prove useful to examine the fluorinated analog of neo-pentane. The choice among these compounds is based largely on physical properties. Some work on these compounds indicates a relative effectiveness in fire suppression of $C_3F_8 \geq C_2F_6 > CF_4$ [48]. For the straight-chain perfluoro compounds the boiling points are -128,-78,-37,-2 for C1 - C4 respectively (temperatures in °C), so that all of them might be considered for total flooding applications. The corresponding heat capacities are 63, 105, 146, 188 J/(K-mole). Data are not available on neo-C_5F_{12}, but the heat capacity should be in the region of 230 J/(K-mole) and the boiling point in the range of 0-10° C. Cyclooctafluorobutane (C_4F_8) has a boiling point of -6° C and a heat capacity of 156 J/(K-mole). (The heat capacity per mole is the proper value to be using for a total flood agent since these compounds will be designed to replace a given volume of room air, and thus a defined number of moles of gas will be delivered. For streaming agents, comparing heat capacity per unit weight, or possibly per unit volume may be more useful.)

In general, the toxicity of the perfluorocarbons is not a serious issue - the primary toxic effect is that of asphyxia; that is, it simply replaces the air. For at least some of the fluorinated compounds, there are other possible problems, cyclooctafluorobutane has been investigated for mutagenic effects, and one of larger fluorinated hydrocarbons, n-C_7F_{16}, has been reported to be mildly toxic via inhalation [139]. Table 1 summarizes the relevant physical property data on the recommended compounds.

b. Photosensitive Compounds

The photon flux in the troposphere falls off dramatically at wavelengths below 300 nm [127] due to the absorption of ozone in the upper atmosphere. For the current commercial halons, this is about the point at which they begin to absorb. The net effect is that photolysis is not an important factor in the destruction of these halons. However, small shifts of the absorption cross section toward the red (longer wavelength) would provide substantial increases in total rates of solar photolysis. Research for refrigerant substitutes has resulted in data indicating that solar photolysis is significant when there are two or more chlorine atoms on the same carbon atom [140]. This can be generalized to say that solar photolysis is important as a destruction pathway whenever there are any two halogens larger than fluorine on the same carbon atom. Only for some methane derivatives - C1 compounds - would the absorption spectrum be shifted far enough toward the red for photolysis to be effective. The suggested compounds are $CBrClF_2$, CBr_2F_2, CF_3CFBr_2. Note that the last is an isomer of halon 2402 which is CF_2BrCF_2Br. Halon 2402 should be carefully re-investigated since it is on the edge of having a tropospheric lifetime short enough to be acceptable.

$CBrClF_2$ is classed as an asphyxiant and is thus not toxic in the normal sense of the word. It has a boiling point of -4° C. The other two compounds suggested are higher in boiling point and thus likely substitutes for the liquid halons. CBr_2F_2 has a boiling point of 22° C and a room temperature vapor pressure of 1.15 atm. These physical properties are almost ideal for a liquid agent, since they insure that there will be a minimum of time for evaporation of the extinguishant after its use. The lifetime for solar pyrolysis in the troposphere for these two compounds has been estimated: for the chloro compound the lifetime is 14-21 years; for the bromo compound 0.9-1.4 years. The ethane derivative CF_3CFBr_2 will probably have a lifetime in the 1 year range also, and its physical properties will be similar to those of halon 2402. A summary of the relevant physical data for these compounds is given in Table 2.

c. Hydrogen-Containing Compounds

This group logically divides into two subgroups. The first contains those compounds which are under active consideration as refrigerant substitutes; the second, bromine-containing compounds. Brominated halocarbons were never used as refrigerants or solvents since the solvation or refrigerant properties that were desired could be achieved without bromination, which adds to the cost and in general reduces the chemical stability. There is, however, a broad body of evidence that bromine adds to the fire suppression capability, so brominated compounds were used for this application. In addition, there are special uses for brominated halocarbons, such as halothane, which is used as an anesthetic. The majority of uses for the halocarbons did not require bromine; and so when non-ozone depleting compounds were sought, simple hydrogen substitution was used. The current set of possible replacement compounds for refrigerants should all be tested for fire suppression potential. These compounds are listed in Table 3 along with relevant physical property data.

TABLE 1. COMPOUNDS WITH NO BROMINE OR CHLORINE

Name	Formula	CASN	Phase	Normal boiling point (nbp °C)	Vapor pressure (atm) (298 K)	Heat capacity (J/K-mol) (298 K)	Heat of vaporization (kJ at nbp)
perfluoromethane	CF_4	75-73-0	gas	-128	na	61	11.6
perfluoroethane	C_2F_6	76-16-4	gas	-78	na	106	16.1
perfluoropropane	C_3F_8	76-19-7	gas	-36	8.69	148	19.7
perfluoro-n-butane	C_3F_{10}	355-25-9	gas	-2	2.63	189	23.2
perfluorocyclobutane	C_4F_8	115-25-3	gas	-6	3.07	156	23.0
trifluoromethane	CHF_3	75-46-7	gas	-82	46.7	51	16.7
pentafluoroethane	C_2HF_5	354-33-6	gas	-48.5	$10^{\dagger}$	94	$20^{\dagger}$
1,1,1,2-tetrafluoroethane	$C_2H_2F_4$	881-97-2	gas	-26.5	$7^{\dagger}$	$87^{\dagger}$	$22^{\dagger}$

†Estimated for this report by authors
na = not available

TABLE 2. PHOTOSENSITIVE COMPOUNDS

Name	Formula	CASN	Phase	Normal boiling point (nbp °C)	Vapor pressure (atm) (298 K)	Heat capacity (J/K-mol) (298 K)	Heat of vaporization (kJ at nbp)
dibromodifluoromethane	CBr_2F_2	75-63-8	gas	-58	15.8	69	17.5
2,2-dibromo-1,1,1,2-tetrafluoroethane	$C_2Br_2F_4$	27336-28-8	liquid	50†	0.4†	116	29†

†Estimated for this report by authors

TABLE 3. COMPOUNDS WITH NO BROMINE

Name	Formula	CASN	Phase	Normal boiling point (nbp °C)	Vapor pressure (atm) (298 K)	Heat capacity (J/K-mol) (298 K)	Heat of vaporization (kJ at nbp)
chlorodifluoromethane	$CHClF_2$	75-45-6	gas	-41	10.1	57	20.2
1,1,1-trichloroethane	$C_2H_3Cl_3$	71-55-6	liquid	74	0.16	93	29.8
2,2-dichloro-1,1,1-trifluoroethane	$C_2HCl_2F_3$	306-83-2	liquid	24	$1^{\dagger}$	102	$26^{\dagger}$
2-chloro-1,1,1,2-tetrafluoroethane	C_2HClF_4	2837-89-0	gas	-12	$4^{\dagger}$	$101^{\dagger}$	$23^{\dagger}$
1,1-dichloro-1-fluoroethane	$C_2H_3Cl_2F$	1717-00-6	liquid	32	$0.5^{\dagger}$	$89^{\dagger}$	$27^{\dagger}$
1-chloro-1,1-difluoroethane	$C_2H_3ClF_2$	75-68-3	gas	-10	3.33	82	22.4

†Estimated for this report by authors

The second group, containing bromine, are chosen to try to examine the role of HBr elimination, to provide H atoms for OH attack, and to examine a range of compounds for toxicological effects. The range of compounds includes some that are simple substitutions of H for F or Br in the current commercial compounds, and some that are extensions in that they are derivatives of propane. These have been chosen so that the properties could later be better adjusted. The compounds are:

C1: CHF_2Br and CHFBrCl

C2: $CF_3CHBrCl$,$CF_2BrCFHCl$,CF_2BrCF_2H,CH_2BrCF_3,$CF_2BrCFHBr$,CF_2BrCH_2Br,CHBrFCH-BrF

C3: $CF_2BrCHFCF_3$,$CF_2BrCH_2CF_2Br$,$CF_2HCBr_2CF_2H$,$CBrF_2CH_2CF_3$.

This list contains a bias, in that most of these compounds are commercially available. Other isomers may turn out to be important when toxicity is considered, but those listed above provide a framework for examining the fire suppression and physical properties of the molecules. Physical property data are given in Table 4.

For comparison purposes, a list of properties for the current commercial halons is included in Table 5. While these compounds are not included explicitly on the final list of potential replacements, it is anticipated that they will be tested concurrently with the compounds appearing on the final list.

C. HALOGENATED KETONES, ANHYDRIDES AND ESTERS

1. Justification for Consideration

Fluorinated carbonyl compounds (with appropriate bromine or chlorine substitution) are considered for the present application because the insertion of a carbonyl group into an organic framework shifts the absorption spectrum of the molecule towards the red. The consequence is that the molecule is more likely to be photolyzed in the troposphere (see section II.C). A typical case is the contrast between the absorption spectra of C_2H_6 and CH_3COCH_3 [141]. For the alkane, absorption does not occur for wavelengths above 155 nm. Acetone, however, has an absorption maximum near 280 nm. Thus, it is not surprising that the absorption spectrum of hexafluoroacetone peaks at 313.0 nm [141]. The mechanism and quantum yields for the photolysis of hexafluoroacetone have been studied by many workers [142,143,144,145]. In order to mimic as closely as possible the fire suppressant properties of compounds such as halon 1301 or halon 2402, a bromine group must be substituted for a fluorine in the structure. This will have the effect of moving the absorption spectrum further into the red.

Spectroscopic information on fluorinated esters and anhydrides does not appear to be available. However the similarities between the absorption and photochemical data for 1,1,1- trifluoroacetone and acetone [145] suggest that the photochemical processes are dominated by the presence of the carbonyl group. Thus the data on the hydrogenated esters and anhydrides indicate that their absorption spectra will not be shifted as much towards the red as the ketones. It will be necessary to verify that photolysis will in fact destroy these compounds in the troposphere. All of these compounds are quite soluble in water. This provides another possible mechanism for destruction or removal of these compounds in the troposphere.

In comparison to compounds without the carbonyl group (ethers and alkanes), the biggest changes in physical properties are lower vapor pressures and correspondingly higher boiling points. There will also be a small increase in the heat capacity. A thorough discussion of the chemical consequences under

TABLE 4. COMPOUNDS CONTAINING BROMINE

Name	Formula	CASN	Phase	Normal boiling point (nbp °C)	Vapor pressure (atm) (298 K)	Heat capacity (J/K-mol) (298°C)	Heat of vaporization (kJ at nbp)
bromodifluoromethane	$CHBrF_2$	1151-62-2	gas	-15	4.4	59	23†
bromochlorofluoromethane	$CHBrClF$	593-98-6	liquid	36	0.5†	63	28†
2-bromo-2-chloro-1,1,1-trifluoroethane	$C_2HBrClF_3$	151-67-7	liquid	50	0.4	104	27.3
2-bromo-1-chloro-1,2,2-trifluoroethane	$C_2HBrClF_3$	354-06-3	liquid	53	0.4†	103	29†
1-bromo-1,1,2,2-tetrafluoroethane	C_2HBrF_4	354-07-4	gas	-5	3.1	86†	23.8
2-bromo-1,1,1-trifluoroethane	$C_2H_2BrF_3$	421-06-7	liquid	26	1†	91†	27†
1,2-dibromo-1,1,2-trifluoroethane	$C_2HBr_2F_3$	354-04-1	liquid	76	0.2†	106†	31†
1,2-dibromo-1,1-difluoroethane	$C_2H_2Br_2F_2$	75-82-1	liquid	93	0.1†	95†	33†
1,2-dibromo-1,2-difluoroethane	$C_2H_2Br_2F_2$	20705-29-7	liquid	102†	0.06†	97†	33†
1-bromo-1,1,2,3,3,3-hexafluoropropane	C_3HBrF_6	na	liquid	50†	0.4†	145†	29†
1,3-dibromo-1,1,3,3-tetrafluoropropane	$C_3H_2Br_2F_4$	460-86-6	liquid	118†	0.04†	138†	35†
2,2 dibromo-1,1,3,3-tetrafluoropropane	$C_3H_2Br_2F_4$	na	liquid	120†	0.03†	137†	35†
1-bromo-1,1,3,3,3-pentafluoropropane	$C_3H_2BrF_5$	460-88-8	liquid	51†	0.4†	133†	29†

†Estimated for this report by authors
na = not available

TABLE 5. CURRENT COMMERCIAL HALONS

Name	Formula	CASN	Phase	Normal boiling point (nbp °C)	Vapor pressure (atm) (298 K)	Heat capacity (J/K-mol) (298 K)	Heat of vaporization (kJ at nbp)
halon 1301	$CBrF_3$	75-63-8	gas	-68	15.8	69	17.5
halon 1211	$CBrClF_2$	353-59-3	gas	-9	2.7	74	22.4
halon 2402	$C_2Br_2F_4$	124-73-2	liquid	47	0.43	128	26.8

combustion conditions will be presented later. At the simplest level the introduction of small amounts of CO from the carbonyl group into a flame is expected to have minimal effects.

2. Past Flame Suppression Measurements

Compounds with a carbonyl group have not been used as fire suppressants [146]. In the Purdue report [25], mention was made of the synthesis of ethyltrifluoroacetate. However, no results on flame suppression properties were given. As can be inferred from the earlier discussion, the exact nature of the fire suppression process is not well characterized. In the following some of the issues will be discussed. The mechanism for the decomposition of the suppressant in a fire situation may be an important property when there is a chemical basis for such activity. Although there are no direct measurements on the mechanisms and rates for the decomposition of these compounds, some estimates can be made [147,148,149]. If the suppressant molecule contains no hydrogen atoms, the general decomposition process will involve the cleavage of the weakest bond [147] and/or hydrogen atom attack on the bromine or chlorine substituent [150,151]. The gradation of bond strengths for the present discussion is C-F > C-Cl ≈ C-C > C-Br [149]. Thus carbon-bromine bonds are the most readily broken in fire situations. Alternatively, hydrogen atoms can abstract chlorine and bromine, leading directly to the formation of the hydrogen halides. This is a much less selective process. At lower temperatures, this is undoubtedly the prime mechanism for removing halides from the organic moieties. The uncertainty regarding the temperature at which chemical suppressant action is effective prevents a definitive choice between these alternatives. Interestingly, it is usually assumed that hydrogen atoms will not abstract fluorine atoms. However, there are almost no experimental tests of this assumption.

The consequence of these considerations is that, if one starts with halon 2402 and inserts a carbonyl group between the carbon-carbon bond, the chemical kinetic stability properties (in terms of unimolecular decomposition to form bromine or hydrogen atom attack leading to hydrogen bromide formation) will not be greatly changed. There are, however, differences from halon 2402 in the nature of the perfluorinated fragments. For halon 2402, perfluoroethylene is formed almost immediately upon removal of the first bromine, whether by radical attack or thermal decomposition. For the carbonyl compounds listed here, their chemical structures suggest the rapid formation of a large variety of perfluorinated compounds and radicals. It is usually assumed that these properties will have no effect on fire suppression capabilities. On the other hand, as noted earlier, Sheinson and coworkers [46,125] claim that the CF_3 radical acts as a chemical flame suppressant. Because some of these compounds are toxic, probably the most important reason for investigating the fire suppressant power of this type of compound is to elucidate the role of the organic fluorine species generated during fire situations.

3. Recommendations

In the absence of any data on the fire suppression properties of compounds containing carbonyl groups, it is worthwhile to examine these compounds in some detail. Table 6 includes the compounds which are recommended for testing along with relevant physical properties. The first five compounds in Table 6 are commercially available. Only one of these compounds contains a bromine group; thus, a true comparison to halons 1301 and 2402 will require custom synthesis of the last two compounds in the table, which contain bromine atoms. Synthesis of these compounds from common materials should not be particularly difficult [152]. Direct comparison of the fire suppression properties of these compounds when bromine is substituted for hydrogen and with the suppression effectiveness of alkanes and ethers should be especially interesting.

All of these compounds have a considerable degree of toxicity. This is probably the chief constraint to their use [139]. It is for this reason that fluorinated acids, aldehydes and acyl compounds have not been included in the list. It may be possible to use these compounds in dilute mixtures in the presence of nonchemical suppressants, such as the perfluorinated compounds. It is suspected that the situation with

TABLE 6. HALOGENATED KETONES, ANHYDRIDES AND ESTERS

Name	Formula	CASN	Phase	Normal boiling point (nbp °C)	Vapor pressure (atm) (298 K)	Heat capacity (J/K-mol) (298 K)	Heat of vaporization (kJ at nbp)
hexafluoracetone	CF_3COCF_3	684-16-2	gas	-26	6.65	118	20.9
trifluoroacetic anhydride	$CF_3COOCOCF_3$	407-25-0	liquid	40	.4†	155†	28.0†
bis(perfluoroisopropyl) ketone	$(iC_3F_7)_2CO$	813-44-5	liquid	73	.15†	280†	29.7†
methyltrifluoroacetate	CF_3COOCH_3	431-47-0	liquid	44	.4†	113†	28.2†
3-bromo-1,1,1-trifluoropropanone	CF_3COCH_2Br	431-25-6	liquid	86	.08†	113†	32.0†
bromopentafluoroacetone	$BrCF_2COOCF_3$	815-23-6	liquid	31	.9†	126†	26.4†
bromomethyltrifluoroacetate	CF_3COOCH_2BR	116587-92-4	liquid	105†	.03†	126†	33.7†

†Estimated for this report by authors

regard to toxicity will not improve appreciably with bromine substitution. Furthermore, bromine substitution will increase the boiling point by 50-60° C.

D. UNSATURATED HALOCARBONS

1. Justification for Consideration

Hydroxyl radicals add readily to double bonds [153] near ambient temperatures to form a hydroxyl-alkyl radical. The newly-formed radical readily reacts with the oxygen in the troposphere and can therefore be destroyed before it is transported into the stratosphere where formation of chlorine and bromine atoms through photolysis will destroy ozone. Rate constants for OH attack on totally halogenated ethylenes are, however, much smaller than for ethylene itself [153]. An important issue will be whether this decrease will move it out of the range necessary for destruction of these molecules in the troposphere. The presence of the double bond and a bromine atom may shift the absorption spectrum of a particular species further toward the red and thus give photolysis [141] a chance to destroy the gas before it migrates into the stratosphere.

The introduction of a double bond leaves physical properties relatively unchanged. There are small decreases in the boiling point and heat capacity; however, profound changes in the possible chemistry can be expected. These are discussed in a subsequent section.

2. Past Flame Suppression Measurements

The Purdue report [25] mentioned that perfluorinated ethylene is combustible and that, in general, unsaturated compounds are ineffective in decreasing the flammability of air and n-heptane mixtures. However, the exact nature of the unsaturated compounds investigated was not specified; and it was found that 2,2-difluorovinyl bromide had suppression properties similar to methyl bromide. Aside from this cursory mention, Larsen [154] has published a table containing data on lower explosion limits for a variety of halogenated organics with possible application as anesthetics. These include a number of olefins. Although exact comparisons are difficult, inspection of the data suggests that the presence of a double bond lowers the flammability limit.

A large number of fluorinated olefins are available. Assuming a special role for bromine in fire suppression, custom synthesis will be necessary to place bromine in a variety of positions and exploit the special effects introduced with the presence of a double bond. A very interesting aspect of these compounds is that, depending on the site of bromination, one can have molecules where the strength of the C-Br bonds will cover a range of nearly a 100 kJ/mol [138,148,149]. This can be contrasted with the situation for halon 1301 and halon 2402 where the difference in bond energies is only 18 kJ/mol. For example, a bromine in the allylic position in a compound such as 3-bromoperfluoropropene will have a carbon-bromine bond strength about 45 kJ/mol lower than that for halon 2402. The bond strength will in fact approach that of the CF_3-I bond. Such a compound can therefore be expected to release bromine atoms through a thermal mechanism with great rapidity.

Even more interesting is the introduction of possible new reaction pathways. Although carbon-bromine bond energies adjacent to double bonds are greatly increased, hydrogen atoms can add to double bonds; and thermodynamics dictates that it will displace all halogens except fluorine atoms [155]. Thermochemistry suggests that OH can displace bromine atoms [156,157]. Alternatively, after addition, the hydrogen halide may be eliminated directly. It is well known that in the pyrolysis of hydrocarbons the formation of olefins is responsible for the observed self-inhibiting nature of most of these systems [158]. The fire suppression capability of difluorovinylbromide can be rationalized in terms of the displacement of the bromine atom by a hydrogen atom. This provides a rapid means of releasing bromine into the combustion region.

3. Recommendations

Table 7 lists the names, formulas, and relevant properties for those compounds which are recommended for study. The first six compounds are commercially available. None contains a bromine group. Therefore, custom synthesis will be necessary to widen the range of possibilities. Based on the earlier comments, the molecules which have been added to Table 7 will be particularly interesting.

Bromine substitution will increase the boiling point. Some of the compounds contain hydrogen. This will render the double bond redundant. The possibility that under certain conditions they may be inflammable must also be considered [25,154].

Many of these compounds are mildly toxic [139] and therefore compare unfavorably with halon 1301. Perfluorinated isobutene is an extremely dangerous poison. It may well be necessary to consider the possibility of its formation during the use of some of the other perfluorinated olefins. Unsaturated olefins such as 1,2-bis(perfluoro-n-butyl)ethylene or bis(di-n-butyl)ethylene have been used as blood substitutes [159,160]. This would seem to assure that these compounds are not toxic. As blood substitutes, these molecules must have low vapor pressures or, equivalently, high boiling points. Thus the boiling point for 1,2-bis(perfluoro-n-butyl)ethylene is 132°C and would seem to disqualify this compound on purely physical grounds. Compounds such as 1,2- bis(perfluoromethyl)ethylene, tetris(perfluoromethyl)ethylene, and those where there is bromine for fluorine or hydrogen substitution will probably have more reasonable boiling points. The important issue is whether such molecules will retain the favorable toxicity profiles. Bagnall and coworkers [161] have synthesized a number of partially-fluorinated butenes with chlorines in the allylic and vinyl positions in order to investigate possible anaesthetic properties. It appears that a vinyl CF_2Cl group leads to unfavorable toxic effects.

The main reason for studying these compounds is to define the role of the double bond. It should be noted that the experimental observations regarding self-inhibition and the lowered explosion limits appear to be contradictory. There are clearly fundamental issues that are not understood. Particularly important experiments are those that involve studies with bromine in a variety of positions. For example, for perfluorinated propene, studies with bromine substitution in the 1 and 3 positions may well lead to the determination of whether the manner or rate by which bromine atoms are released into a fire situation is of any consequence.

E. HALOGENATED ETHERS AND RELATED COMPOUNDS

1. Justification for Consideration

The addition of an oxygen between two carbon groups in an alkane moves the absorption spectra about 30 nm toward the red [141]. This suggests that for a compound such as CF_2BrCF_2Br or $CF_3CFClBr$, oxygen insertion may be sufficient to make it photochemically active [136]. The chances of ethers with only one bromine or chlorine atoms being photochemically active in the appropriate spectral region is much less likely. The addition of an extra CF_2 group is not expected to improve the situation. The effect of hydrogen substitution will probably be similar to that in the current commercial halons with respect to reactivity towards OH attack.

Some of the compounds in this class are well known anesthetics [162,163,164,165]. These include methoxyflurane ($CHCl_2CF_2OCH_3$), enflurane (CHF_2OCF_2CHFCl), and isoflurane ($CF_3CHClOCHF_2$).

TABLE 7. UNSATURATED HALOCARBONS

Name	Formula	CASN	Phase	Normal boiling point (nbp°C)	Vapor pressure (atm) (298 K)	Heat capacity (J/K-mol) (298 K)	Heat of vaporization (kJ at nbp)
perfluoropropene	C_3F_6	116-15-4	gas	-29	6.42	116	21
perfluorobutene-2	C_4F_8-2	360-89-4	gas	0	2.62	138[†]	21[†]
perfluorotoluene	$CF_3C_6F_5$	434-64-0	liquid	104	.03[†]	207	34[†]
1,1,3,3,3-pentafluoropropene-1	$CF_3CH{=}CF_2$	690-27-7	gas	-21	5[†]	109[†]	23[†]
3,3,3-trifluoropropene	$CF_3CH{=}CH_2$	690-27-7	liquid	-17	4[†]	92[†]	24[†]
1,2-bis(perfluoro-n-butyl)ethylene	$(n\text{-}C_4F_9)CH{=}CH(n\text{-}C_4F_9)$	8455143-9	liquid	132	.006[†]	377[†]	36[†]
3-bromoperfluoropropene	$BrCF_2CF{=}CF_2$	431-56-1	liquid	28[†]	1[†]	121[†]	27[†]
1-bromoperfluoropropene	$CF_3CF{=}CFBr$	14003-53-33 14003-61-3	liquid	30[†]	1[†]	121[†]	27[†]
1,2-bis(perfluoromethyl)ethylene	$CF_3CH{=}CHCF_3$	66711-86-2	liquid	6[†]	1.6[†]	130[†]	26[†]
1-bromoperfluoromethyl-2-perfluoromethylethylene	$CF_2BrHC\text{-}CHCF_3$		liquid	57[†]	0.1[†]	138[†]	30[†]
1-bromo-bis(perfluoromethyl)-ethylene	$CF_3BrC{=}CHCF_3$	400-41-9	liquid	65[†]	.06[†]	143[†]	33[†]
tetris(perfluoromethyl)ethylene	$(CF_3)_2C{=}C(CF_3)_2$	360-57-6	liquid	55	.28[†]	180[†]	29[†]

[†] Estimated for this report by authors

It is claimed that they are non-flammable. This is however only with reference to their specific application. Larsen [154] has shown that their lower flammability limits for oxygen are only at the 5 to 7 percent level. This can be compared with a value of 10 percent for methyl bromide. The large number of studies on the use of fluorinated compounds as anesthetics provides a very important initial source of toxicity data [154,161,164,165,166,167]; however, these data should be used with care, since much of the focus is on short-term effects. A disturbing property of the ethers is their wide range of (generally unpredictable) biological responses. Hexafluorodiethyl ether, for example, is an extremely potent convulsant. Perfluorodiethyl ether is, however, only mildly toxic. Of course, a good anesthetic is an undesirable fire suppressant. Indeed, the ratio of concentrations necessary for satisfactory anesthesia and lethal dosage is rarely an order of magnitude [154]. Perfluorinated n-butyltetrahydrofuran has been used as a blood substitute. Certainly this application should provide a very satisfactory guarantee of safety. A high priority should be assigned to the bromination of the perfluorotetrahydrofuran.

Physical properties of the ethers are quite favorable. The boiling points appear to be little changed with the substitution of the oxygen.

The above discussion has focused on C, F, H, and O compounds. Some consideration has also been given to halogenated organic systems involving sulfur and nitrogen atoms. The specific compounds are the perfluorinated thioethers and amines. Although the absorption spectra of these compounds probably do not extend sufficiently far toward the red for photolysis to be an effective destruction mechanism in the troposphere [141], a particularly interesting aspect of their behavior is the possibility of addition of OH to the sulfur or nitrogen moiety followed by reaction with oxygen and subsequent removal from the troposphere. The evidence for such a process is quite strong for the organic sulfides [168] and less compelling for the amines where there are insufficient data.

The sulfur analog of the well known anaesthetic methoxyflurane has been synthesized and it appears to be a much more powerful anaesthetic. This suggests that sulfur substitution may well have deleterious toxic effects in comparison to the ether. However it is known that bis(trifluoromethyl) sulphide resembles a perfluoro ether in its stability to heat and attack by strong acids and bases [169]. Tris(perfluorinated propyl) amine is used as a blood substitute. It can therefore be assumed that there will be no toxicity problems. It also suggests that smaller members of this group will have similar properties. This is borne out by the inertness of tris(perfluoromethyl) amine [170].

2. Past Flame Suppression Measurements

Malcolm [6] has noted rough flame suppression studies with octadecafluoroperdibutyl ether. On a relative basis it is only half as effective as carbon dioxide. This is difficult to understand since the heat capacity of the perfluoro compound is much larger than that for CO_2. There does not appear to have been any other prior work using halogenated species containing ether linkages as fire suppressants [25]. The strengths of the carbon-bromine bonds are expected to be in the same range as halon 1301 and halon 2402. Perfluorinated phosgene as well as various fluorinated carbenes and methyl radicals are expected to be formed quite readily. Experimental studies will therefore bear on the question of the importance of such substitutions for the CF_3 and C_2F_4 from halon 2402 and halon 1301 decomposition. Although it has been noted earlier that the three anesthetic ethers are not really non-flammable in the general sense, it may well be that bromination will improve this property.

3. Recommendations

The compounds listed in Table 8 are recommended for study. The first five compounds are commercially available and may also be useful as possible reactants for subsequent synthetic work. With EPA support, bis(bromodifluoromethyl) ether and 1-bromo-1,1,3,3,3- pentafluorodimethyl ether are now being

TABLE 8. HALOGENATED ETHERS AND RELATED COMPOUNDS

Name	Formula	CASN	Phase	Normal boiling point (nbp °C)	Vapor pressure (atm) (298 K)	Heat capacity (J/K-mol) (298 K)	Heat of vaporization (kJ at nbp)
tetrafluorodimethyl ether	CF_2HOHCF_2	1691-17-4	gas	2	2[†]	92[†]	24.5[†]
pentafluorodimethyl ether	CF_2HOCF_3	3822-68-2	gas	-35	7[†]	109[†]	21.2[†]
2-chloro-1-(difluoromethoxy)-1,1,2-trifluoroethane	CHF_2OCF_2CHFCl	13838-16-9	liquid	56.5	.29	162[†]	29.4[†]
isoflurane	$CF_3CHClOCHF_2$	26775-46-7	liquid	48.5	.32	167[†]	28.7[†]
perfluoro-2-butyltetrahydrofuran	$C_4F_9C_4F_7O$	335-36-4	liquid	103	.033[†]		33.5[†]
bis(bromodifluoroethyl) ether	CF_2BrOCF_2Br	na	gas	25[†]	1[†]	117[†]	26.7[†]
1-bromo-1,1,3,3,3-pentafluorodimethyl ether	CF_2BrOCF_3	na	gas	-30[†]	6[†]	104[†]	24.7[†]
bromoenflurane	$CBrF_2OCF_2CHFCl$	na	liquid	67[†]	2[†]	175[†]	30.3[†]
octafluorofuran	C_4F_8O	773-14-8	liquid	50[†]	.33[†]	151[†]	28.8[†]
3-bromoperfluorofuran	BrC_4F_7O	na	liquid	105[†]	.03[†]	159[†]	33.7[†]
bis(perfluoromethyl) thioether	CF_3SCF_3	371-78-87	gas	-22.2	6.1	126[†]	25.1[†]
tris(perfluoromethyl) amine	$(CF_3)N$	432-03-1	gas	-10.1	3.9	167[†]	25.1[†]

[†] Estimated for this report by authors
na = not available

synthesized. The same procedures should lead to the bromination of the enflurane and isoflurane. Perfluoro-2-butyltetrahydrofuran is included because of its use as a blood substitute. This is a large compound and its boiling point and vapor pressure are unfavorable. Thus it will be important to test the tetrafluorofuran and 3-bromotetrafluorofuran.

The first prerequisite will be to establish that the simplest brominated ethers can in fact be photolytically decomposed. Comparison of these compounds with the purely fluorinated analogs will be extremely interesting not only for the immediate problem, but to develop a better understanding of fire suppression mechanisms. For example, comparisons of the behavior of bis(bromodifluoromethyl) ether with halon 2402 and 1,3-dibromo-1,1,2,2,3,3-hexafluoropropane should yield a great deal of information on mechanistic issues. It is interesting that enflurane (CHF_2OCF_2CHFCl) has apparently lower toxic effects in comparison to halothane ($CF_3CHClBr$) and has overtaken the use of the latter as the most used volatile anesthetic agent in many institutions, despite the higher cost [162]. It is possible that the greater toxicity of the halothane is due to the presence of the bromine group. This is an issue that should be investigated.

For the nitrogen and sulfur compounds, it will be extremely interesting to investigate bis(perfluoromethy) sulfide and tris(perfluoromethyl) amine, and, should the initial results be favorable, to go on to compounds where bromine is substituted for fluorine. These compounds are not available from commercial sources. However, the standard electrochemical method (Simons process) [171] is probably suitable for their preparation. This process has, in fact, been used to prepare some of the amines [170,172]. It is also very convenient that fluorination is not complete. There will, therefore, be a few hydrogens remaining for bromination. The sulfide can also be prepared from the pyrolysis of the disulfide [173].

F. HALONS CONTAINING IODINE

1. Justification For Consideration

Current commercial flame suppressants such as halons 1211 and 1301 include bromine atoms. Many experts in the field (e.g., [57,72,146] have reported the efficiency of halogen atoms for fire suppression as follows:

$$I > Br > Cl > F.$$

Some compounds containing iodine were investigated in the Purdue study [25]. Malcolm [6] used these findings to assign "apparent atomic values of firefighting effectiveness" for the halogens. His results were: fluorine, 1; chlorine, 2; bromine, 10; and iodine, 16. Later work showed that extinguishing concentrations of halons containing F, Cl, and Br were correlated accurately in terms of scores obtained simply by summing the products of the number of each halogen atom in the molecule by its firefighting effectiveness [97]. Unfortunately, no molecules containing iodine were tested during the development of this correlation.

Despite the apparent effectiveness of iodine atoms for flame inhibition, no compounds containing iodine have been widely used or tested for flame extinguishment purposes. References in the early literature of the field [1,5] suggest that halons containing iodine were not considered primarily due to the scarcity and cost of iodine; it is also clear that the recognition that iodine compounds are generally more toxic played a role [1].

In general, iodine-containing halons are more reactive and have longer wavelength absorptions than analogs containing lower molecular weight halogens. These characteristics suggest that molecules containing iodine will be more easily destroyed in the troposphere than the corresponding bromine compounds. As a result, they are less likely to reach the stratosphere where they would contribute to the destruction of ozone.

Based on the above discussion, it is considered likely that halons containing iodine will have good fire suppression capabilities while being less damaging to stratospheric ozone than the current commercial halons. In addition to this practical reason for including a number of compounds containing iodine on the final list, it is also likely that new principles for the understanding of chemical fire suppression will emerge following the testing of a number of these species.

2. Past Flame Suppression Measurements

One very short, but intriguing reference, suggests that iodine-containing compounds may be very effective extinguishment agents for real fires [174]. de C. Ellis refers to early work of R.V. Wheeler and H.B. Dixon who, it is claimed, discovered "the combustion-inhibiting influence of the iodides" [174]. Measurements were made to test the effectiveness of methyl iodide as compared to carbon tetrachloride, the commonly-used chemical fire extinguisher of the day. Results indicated that only one fifth of the quantity of CH_3I was required to extinguish a fire. Tests are described for petrol burning on water with an indication that burning areas greater than 1.3 m^3 were used. Carbon tetrachloride sprayed on the fires failed to extinguish; but when methyl iodide was used, the flames were quickly quenched.

Some common measurements of suppression effectiveness have been reported for iodine-containing compounds. In 1932 Jorissen et al. [118] reported the flammability limits for methane-air mixtures inhibited by ethyl iodide. The peak concentration was slightly greater than 5 percent. Flammability peak concentrations for CH_3I (6.2 percent) and C_2H_5I (6.2 percent) in n-heptane/air mixtures were determined during the Purdue investigation [25]. Both agents required considerably lower concentrations to inert n-heptane/air mixtures than the corresponding species with bromine. The peak concentrations were somewhat higher than for fully-halogenated alkanes. Lask and Wagner reported the effects of CF_3I on the flammability limits of n-hexane/air mixtures [79]. The peak concentration for this compound was roughly 3.5 percent.

Rosser et al. [78] have reported measurements of reductions in flame speeds for methane/air mixtures due to the addition of a number of compounds including CH_3I and C_3H_7I. Their results indicated that the compounds containing iodine are roughly equivalent to their analogs containing bromine in fire suppression effectiveness. Homann and Poss measured reductions in flame speed as various additives were added to ethylene/air mixtures [81]. Measurements were recorded as a function of pressure. Direct comparisons were made for CH_3I and CH_3Br acting as inhibitors. For a range of pressure, the methyl iodide was found to inhibit the flame slightly more efficiently.

Flame speeds for a one-dimensional ethylene/air premixed flame with 1 percent concentrations of various agents added have been calculated by Westbrook utilizing a detailed chemical kinetics model [86]. Agents included were HCl, HBr, HI, and methyl, ethyl, and vinyl radicals combined with Cl, Br, or I. The addition of the agents to the fuel/air mixture resulted in significant reductions in calculated flame speeds, with the relative reductions increasing in the order $I \approx Br > Cl$. These results suggest that species containing iodine should be effective fire suppressants.

Sheinson et al. [46,125] have reported cup burner results for heptane fuel in which the concentrations of agent in air required to extinguish the flame were measured for a number of compounds including CF_3Br (3.1 percent) and CF_3I (3.2 percent). These two compounds yielded the lowest percentages of the compounds tested in this study. As is clear from the values reported, the effectiveness of these two similar compounds were nearly identical with perhaps a slight edge going to the agent containing bromine.

A few workers have investigated the effects of agents containing iodine on fires. The work of de C. Ellis [174] was described above. Malcolm [56] quotes the results of two relevant studies. One investigation was performed by the Civil Aeronautics Authority in Indianapolis, IN (See Appendix E, Exhibit 1 in Malcolm [56]). Fires in a model aircraft engine were extinguished by a variety of agents and the amount required for extinguishment reported as a weight. On a per mole basis, the amounts of methyl iodide and methyl bromide required were identical. The second study quoted was work performed at the Minnesota Mining and Manufacturing Company and is summarized in Malcolm's Appendix E, Exhibit 2 [56]. In this study flaming cotton was inserted into a small enclosure in which the inhibitor had been mixed with air and the amount of agent required for extinguishment measured. One of the gases tested in this way was methyl iodide. On a per mole basis the most effective agent tested was the halon with iodine. The agent CB (halon 1011) was one of the molecules included in this investigation. The methyl iodide was roughly 10 percent more effective than this agent.

3. Recommendations

The fire suppression properties, as well as other relevant properties of halons with iodine atoms, have not been well-characterized despite indications that such compounds are very effective flame suppressants. A wide range of such compounds is included on the list in order to provide insight into fire suppression mechanisms and to investigate whether such compounds might be used as replacements for existing clean firefighting agents. Appropriate testing of these compounds is likely to provide significant insights into the effects of replacing bromine with iodine on the ODP and toxicity behaviors of halons.

As a direct test of the effectiveness of compounds containing iodine compared to the three widely employed halons (1211, 1301, and 2402), four analogs of these compounds with iodine substituted for one or more of the bromine atoms are included on the list. In order to characterize the behavior of hydrocarbons with a single substituted iodine atom, the homologous series with 1-3 carbons has been added. Finally, a perfluorinated propyl iodide has been included to characterize the effect of substituting fluorines for hydrogens on the alkyl iodides fire suppression characteristics. The resulting list of compounds is given in Table 9, along with appropriate physical properties.

G. SULFUR HALIDES

1. Justification for Consideration

a. Parent Properties

Sulfur halides are identified as possible fire suppressants, based principally on the properties of one member of this class of compounds -- SF_6. This gas has many desirable properties for a chemical fire suppressant. It is colorless, odorless, tasteless, nontoxic, and nonflammable [175]. Since SF_6 contains numerous fluorine atoms, the molecule might be expected to have significant fire suppression capability.

b. Chemical Analogs

SF_6 is a unique molecule due to its high symmetry and strong bonds. The other sulfur halides are toxic, reactive, and thermally unstable. As noted above, this is not the case for SF_6. Normal nucleophilic reagents cannot attack the highly symmetric octahedral structure [175].

One might hope that it would be possible to exchange one or more of the fluorine atoms on SF_6 for chlorine or bromine to create a gas with properties similar to SF_6, but with improved fire

TABLE 9. RECOMMENDED HALONS CONTAINING IODINE

Name	Formula	CASN	Phase	Normal boiling point (nbp °C)	Vapor pressure (atm) (298 K)	Heat capacity (J/K-mol) (298 K)	Heat of vaporization (kJ at nbp)
iodotrifluoromethane	CF_3I	2314-97-8	gas	-22.5	na	70.9	$22^\dagger$
chlorodifluoroiodomethane	CF_2ClI	420-49-5	liquid	33	na	$76^\dagger$	$27^\dagger$
1-bromo-1,1,2,2-tetrafluoro-2-iodoethane	CF_2BrCF_2I	421-70-5	liquid	78	na	$124^\dagger$	$31^\dagger$
1,1,2,2-tetrafluoro-1,2-diiodoethane	CF_2ICF_2I	354-65-4	liquid	112	na	$126^\dagger$	$34^\dagger$
iodomethane	CH_3I	74-88-4	liquid	42.4	0.53	44.1	27.4
iodoethane	CH_3CH_2I	75-03-6	liquid	72.3	0.18	67.8	29.4
1-iodopropane	$CH_3CH_2CH_2I$	107-08-4	liquid	102.4	0.06	88.3	32.1
1,1,1,2,2,3,3-heptafluoro-3-iodopropane	$CF_3CF_2CF_2I$	754-34-7	liquid	41	na	$197^\dagger$	$28^\dagger$

†Estimated for this report by authors
na = not available

suppression capabilities. Unfortunately, this does not turn out to the case. Only two analogs, SF_5Cl and SF_5Br, are stable. The molecular properties of these species differ dramatically from those of the parent molecule. SF_5Cl is stable up to 400° C while SF_5Br decomposes at 150° C [176]. Both are easily hydrolyzed. SF_5Cl has been reported in rat studies as a strong lung irritant and as being as toxic as phosgene [177].

2. Past Flame Suppression Measurements

Three references were identified which report the mole fraction of SF_6 at the flammability peak (concentration just sufficient to limit flame propagation for all concentrations) for hydrocarbon/air flames. The Purdue study [25] found that a mole fraction of 0.205 was required to inhibit n-heptane/air flames. This was one of the higher limit concentrations reported of the 56 compounds investigated. A similar investigation for pentane/air mixtures yielded a mole fraction of 0.158 [82]. Compared to the levels of CO_2 necessary for these cases, SF_6 appears to be slightly more effective for pentane combustion than for n-heptane, but relatively high mole fractions of SF_6 are required for extinguishment with each fuel.

A low-pressure premixed CH_4/air flame only required a mole fraction of 0.057 SF_6 to cause extinguishment [178]. This mole fraction is somewhat lower than found in the atmospheric-pressure flame studies, but it is difficult to reach conclusions since the amounts of other gases required to extinguish the low-pressure flame were also smaller than found for the corresponding atmospheric-pressure flames.

Sheinson et al. [45,46] have investigated the effectiveness of SF_6 as a flame extinguishment agent in a cup burner apparatus with n-heptane fuel. Their results and analysis indicate that the only mechanism responsible for flame suppression with SF_6 is the physical effect based on the molecular heat capacity.

The only fire suppression investigation of halogen-substituted SF_6 compounds identified was the work of Sheinson et al. [45,46] These workers measured the amount of SF_5Cl and SF_6Br required to extinguish n-heptane flames. Their analysis suggests that SF_5Cl has no chemical suppression capability and may actually enhance combustion. On the other hand, SF_5Br appears to have a definite flame suppression capability.

3. Recommendations

SF_6 is readily available commercially. SF_5Cl is also produced by specialty manufacturers. No commercial source of SF_5Br has been identified, but an effective procedure for its preparation has been published [179] and it should be possible to synthesize this molecule at a reasonable cost for testing purposes.

Since a consensus does not exist on the fire suppression capabilities of SF_6, this molecule should definitely be included on the list for testing. Clearly, SF_5Cl and SF_5Br are not suitable as replacements for the current commercial halons. However, it seems likely that the understanding of fire suppression mechanisms can be significantly enhanced if these compounds are included in the testing protocol. It is recommended that SF_5Cl, SF_5Br and SF_6 be included on the list of test compounds. Relevant properties are included in Table 10.

H. COMPOUNDS CONTAINING PHOSPHORUS

1. Justification for Consideration

Phosphorus-containing compounds are widely used as fire retardants for natural and man-made polymers [146]. This suggests that gas-phase phosphorus compounds could prove to be effective flame

TABLE 10. RECOMMENDED SULFUR HALIDES

Name	Formula	CASN	Phase	Normal boiling point (nbp °C)	Vapor pressure (atm) (298 K)	Heat capacity (J/K-mol) (298 K)	Heat of vaporization (kJ at nbp)
sulfur fluoride	SF_6	2551-62-4	gas	-63.8 (sub)	21.8	97.0	23.6
sulfur chloride fluoride	SF_5Cl	13780-57-9	gas	-21	na	104	21.7
sulfur bromide fluoride	SF_5Br	15607-89-3	gas	3.1	na	107	24†

†Estimated for this report by authors
na = not available

extinguishment agents. It is generally believed that antimony halides are effective radical traps [146] and thus act as flame suppressants. Since phosphorus and antimony are both group V elements, a similar behavior might be expected for phosphorus trihalides.

2. Past Flame Suppression Measurements

An immense literature exists which deals with the use of phosphorus-containing compounds as flame retardants in solids [146]. However, only a few references have been identified in which the effectiveness of a phosphorus-containing liquid or gas as a flame suppressant has been tested. Phosphorus trichloride was included as one of a large number of compounds tested for fire-suppression capabilities during the study carried out at Purdue University [25]. Results for this study are reported in terms of the volume percent of the tested molecule required to prevent flame propagation in heptane/air mixtures. PCl_3 required one of the highest volume fractions, 22.5 percent, of any species studied during this investigation. Of the 56 compounds considered in the Purdue study, only CO_2, CF_4, and HCl required higher volume fractions to prevent flame propagation.

Lask and Wagner [79] measured the concentrations of a variety of species required to reduce the flame velocity of a n-hexane/air flame by 30 percent. Included in the tests were PCl_3, PBr_3, $PSCl_3$, and $PSBr_3$. These compounds were all found to be considerably more effective inhibitors than Cl_2, Br_2, or CCl_4. These authors concluded that the phosphorus compounds inhibit flames by a second chemical mechanism which occurs in conjunction with the mechanism responsible for flame inhibition due to halogen molecules.

$POCl_3$ was one of the molecules Miller tested for extinguishment of low-pressure premixed flames of methane [178]. A considerably lower mole fraction of $POCl_3$ than Br_2, which is recognized as an effective suppressant, was required for extinguishment. Jorissen et al. [118] also noted that $POCl_3$ is a very powerful flame inhibitor. They claimed that less than 1 percent of this compound is sufficient to prevent flame propagation in methane/air mixtures.

The papers summarized above suggest that some phosphorus-containing molecules may be very efficient fire suppression agents. At the present time, the fire suppression behavior of this family of molecules must be classed as poor. Investigation of the fire suppression behavior of phosphorus-containing molecules is certain to result in an improved understanding of chemical fire suppression mechanisms and might point the way to possible replacements for the current commercial halons.

3. Recommendations

Only a relatively few liquids and gases containing phosphorus are known [180,181]. These compounds are the hydrides, trihalides, pentahalides, and oxo-halides. In addition, the phosphonium halides have been observed. Most of the compounds are highly toxic and hygroscopic. For this reason they are poor candidates for widespread replacement of existing halons. However, it is possible that one or more of these compounds may provide important tests for the screens being developed or new insights into flame extinguishment mechanisms. A choice of appropriate compounds for screen testing is aided by the information in Table 11 [181,182,183,184]. Only a few of these compounds are available commercially. These include PCl_3, PBr_3, $POCl_3$, $PSCl_3$, PH_3, and PCl_5.

Based on previous results of fire suppression investigations and the information shown in Table 11, the compounds included in Table 12 have been chosen for inclusion on the final list of compounds. These compounds should allow conclusions concerning the role of phosphorus in fire suppression effectiveness to be formulated. Comparison between the results for the phosphorus halides and the phosphoryl halides will allow the fire suppression effectiveness of these two families of phosphorus compounds to be characterized. Finally, by comparing findings for cases where different halogen atoms are substituted on the phosphorus, the

TABLE 11. PHOSPHOROUS-CONTAINING GASES AND LIQUIDS

Compound	m.p. (°C)	b.p. (°C)	Comments
PH_3	-209	-126	Highly flammable, can form explosive mixtures
PH_4Cl	28	subl	This compound is very unstable
PH_4Br	≈30	subl	This compound is very unstable
PH_4I	≈19	39	This compound is very unstable
PF_3	-152	-102	Complexes with hemoglobin, hydrolyses slowly
PCl_3	-112	76	Violently hydrolyzed by water
PBr_3	-40	173	Violently hydrolyzed by water
PF_2Cl	-165	-47	
$PFCl_2$	-144	14	
PF_2Br	-134	-16	
$PFBr_2$	-115	78.4	
PF_5	-136	-121	Very hazardous due to hydrolysis by water
POF_3	-39	-40	
POF_2Cl	-96	3	
$POFCl_2$	-80	53	
POF_2Br	-85	32	
PSF_3	-149	-52	
$PSCl_3$	-35	125	
PSF_2Br	-137	36	

TABLE 12. RECOMMENDED PHOSPHOROUS-CONTAINING COMPOUNDS

Name	Formula	CASN	Phase	Normal boiling point (nbp °C)	Vapor pressure (atm) (298 K)	Heat capacity (J/K-mol) (298 K)	Heat of vaporization (kJ at nbp)
phosphorous trifluoride	PF_3	7783-55-3	gas	-101	66	58.7	14.6
phosphorous trichloride	PCl_3	7719-12-2	liquid	+76	.16	71.6	30.5
phosphorous bromide difluoride	PF_2Br	15597-40-7	gas	-16	4.5	$64^{\dagger}$	23.9
phosphoryl fluoride	POF_3	13478-20-1	gas	-40	13.2	68.8	22.1
phosphoryl chloride	$POCl_3$	10025-87-3	liquid	106	.05	84.9	33.7
phosphoryl bromide fluoride	POF_2Br	14014-18-7	liquid	32	.77	$75^{\dagger}$	29.7

†Estimated for this report by authors

importance of chemical flame suppression due to halogen molecules to the overall suppression efficiency of this class of molecules can be assessed.

I. SILICON AND GERMANIUM FLAME INHIBITORS

1. Justification for Consideration

a. Family of Chemicals

The focus of this section is on the compounds of silicon (Si) and, to a lesser extent, on some germanium (Ge) analogs. Two of the other Group IVA elements, tin (Sn) and lead (Pb), are more appropriately classified as metals. Accordingly, compounds involving these elements will be considered in the section on metallic flame inhibitors (Section J).

b. Properties

The position of silicon directly below carbon in the periodic table suggests that the chemistry of these elements will be similar. Like carbon, silicon has a valency of four. There do not appear to be any compounds derived from the divalent state ($3s^2 3p^2$) which are stable at room temperature [188]. However, the tendency to form divalent compounds increases with atomic weight so that Sn(II) and Pb(II) are relatively common. The Group IVA elements, other than carbon, do not form strong bonds with like atoms. The Si-Si bond, for example, is notably weaker (213 kJ/mole) than the Si-C bond (301 kJ/mole).

All of the Group IVA elements form stable halides. The silicon and germanium analogs of the halons, in particular, would be expected to be effective flame inhibitors. This hypothesis was confirmed very early, at least with respect to silicon tetrachloride ($SiCl_4$), which was one of the chemicals tested in the Purdue Research Foundation study [25].

Obviously, if both families of chemicals behaved similarly with respect to all properties, including ozone depletion and global warming potentials, there would be no reason to continue this discussion. There are, however, significant differences in the behavior of these compounds in the atmosphere. Unlike the halons, all of the halosilanes readily hydrolyze in moist air [185]. An important consequence is that these compounds will undergo rapid decomposition in the troposphere and would therefore be expected to have correspondingly low potentials for ozone depletion and global warming. Unfortunately, this beneficial property is offset by the fact that hydrogen halides are produced in the hydrolysis of halosilanes. This effect is so pronounced that the presence of a single silicon-halogen bond in a molecule is sufficient to make its vapors corrosive and dangerous to breathe [185].

On the basis of this consideration, it is clear that along with fire suppression effectiveness, the propensity for hydrolysis will be the critical factor in determining whether any of the halosilanes will be viable candidates for the replacement of halons. The strategy, therefore, is to examine the chemical properties of these molecules in an effort to identify structural permutations which result in a balance between toxicity and tropospheric lifetime, while at the same time retaining their ability to inhibit flames.

2. Past Flame Suppression Measurements

A list of the results obtained by the Purdue Research Foundation [25] is duplicated in Lyon's book on fire retardants [146] and in a review article by McHale [66]. The tabulated values are the volume percent of inhibitor corresponding to the peak in the flammability curve for a premixed n-heptane flame. The value reported for $SiCl_4$ was 9.9 percent. On the basis of this criterion, the flame suppression efficiency of

$SiCl_4$ is between those for halon 1301 (CF_3Br) and carbon tetrachloride (CCl_4), which were found to have peak values of 6.1 percent and 11.5 percent, respectively.

In an independent study, Lask and Wagner conducted flame velocity measurements for a series of additives including some halosilanes and related compounds [79,186,187]. The figure of merit was the volume percent of inhibitor required to reduce the burning velocity of a premixed (stoichiometric) n-hexane flame by 30 percent. On this basis, it was determined that the flame inhibition activity of $SiCl_4$ (0.56 percent) was comparable to Br_2 (0.7 percent) but considerably higher than CCl_4 (1.38 percent).

It is difficult to make quantitative comparisons between data obtained from flammability curve and flame velocity measurements; however, the relative rankings of the inhibitor efficiencies would appear to be consistent. Thus, in addition to the compounds cited above, both sets of measurements have been made on chloroform ($CHCl_3$). The Purdue Research Foundation reported that the peak in the $CHCl_3$ flammability curve occurred at 17.5 percent. This implies that it is a less efficient inhibitor than either $SiCl_4$ or CCl_4. The data on flame speeds justify a similar ranking. Lask and Wagner found that it took 1.97 percent of $CHCl_3$ (in the mixture of fuel and oxidizer) to reduce the velocity by 30 percent of the value obtained for the clean flame. This was considerably more than the amounts of $SiCl_4$ and CCl_4 which were required to achieve the same velocity reduction.

A smaller effect was observed for the silicon analog of chloroform - trichlorosilane ($SiHCl_3$). It required 2.9 percent of this halosilane to reduce the flame speed by 30 percent. Although this is considerably larger than the values obtained for some of the other halogenated compounds, it still indicates a significant degree of flame inhibition. Mixtures of 6.8 percent CO_2, which is widely used as fire extinguishing agent, and 8 percent of N_2, were needed to produce the same degree of inhibition.

Flame velocity measurements were also reported by Lask and Wagner on two additional tetrachlorides of the Group IVA elements. The values of 0.50 percent and 0.19 percent were reported for $GeCl_4$ and $SnCl_4$, respectively. The hierarchy for inhibition: $SnCl_4 > GeCl_4 > SiCl_4 > CCl_4$ was also found to apply to increases in the ignition temperatures of hydrocarbon/($O_2 + N_2$) mixtures [187]. No explanation for this trend has been found; however, it may have some relevance to the problem of interest. It is known that the susceptibility to hydrolysis of compounds involving Group IVA elements decreases with increasing atomic weight [188]. Thus, the most potent inhibitors may, in fact, be the least corrosive. Unfortunately, the drop-off may not be fast enough to yield practical benefits. Thus, $SnCl_4$ readily hydrolyzes and, as a consequence, it is highly corrosive [139]. On the other hand, lead chloride ($PbCl_2$), which does not hydrolyze, is a solid. The toxicity of this compound is probably due more to the presence of a heavy metal than to HCl. The possibility that some of the mixed halogermanes may be more suitable, however, should not be dismissed out of hand.

The mechanism by which the halosilanes affect flame inhibition is probably similar, if not identical, to the halons (vide-supra). The same mechanism, however, cannot explain the flame inhibition which has been observed for tetramethylsilane ($Si(CH_3)_4$) [79,186,187]. This compound, which is commonly referred to as TMS, is routinely used as a standard in nuclear magnetic resonance (NMR) spectroscopy. Although TMS does have a large heat capacity, the effect is considered to be insufficient to explain the degree of flame inhibition exhibited by this compound [189]. The magnitude of flame inhibition suggests, instead, that a chemical mechanism is operant. One possibility is that the alkyl groups play a role in promoting radical recombination of H and OH radicals in the flame. Lask and Wagner reported that a mixture of 1.5 percent of TMS was required to reduce the velocity of their stoichiometric n-hexane flame by 30 percent. This indicates that the inhibiting effect of TMS is comparable to that of CCl_4. The possibility that halogenation of alkyl groups may increase the ability of alkysilanes to inhibit flames should be examined further.

3. Recommendations

Many compounds of the Group IVA elements, including the halosilanes, halogermanes and alkylsilanes are effective flame inhibitors. The possibility that some of these compounds may be viable candidates for the replacement of halon fire extinguishing agents warrants further consideration.

A variety of halogenated and alkylated compounds of silicon and germanium are listed, along with some of their relevant properties in Table 13 [190,191]. These particular compounds were selected because they were thought to represent structural permutations which are likely to affect susceptibility to hydrolysis and flame-inhibition activity. We recommend conducting corrosion and fire suppression efficiency testing of these compounds. This information will be useful in identifying silicon and germanium compounds which are viable alternatives for the existing halon extinguishing agents.

J. METALLIC FLAME INHIBITORS

1. Justification for Consideration

The ability of alkali metal compounds to extinguish fires has been recognized for over 100 years [32]. Sodium hydrogen carbonate ($NaHCO_3$) was probably the first dry chemical extinguishing agent. In addition to $NaHCO_3$, formulations based on potassium hydrogen carbonate ($KHCO_3$), potassium chloride (KCl) and potassium oxalate ($K_2C_2O_4.H_2O$) are now in widespread use as extinguishing agents. More recently, it was discovered that certain heavy metal compounds, including tin chloride ($SnCl_4$), titanium chloride ($TiCl_4$), tetraethyl lead ($Pb(C_2H_5)_4$), chromyl chloride (CrO_2Cl_2) and iron pentacarbonyl ($Fe(CO)_5$) are extremely effective flame inhibitors [189].

Metallics have physical and chemical properties which would seem to disqualify them from consideration as candidates for the replacement of halons. Since these compounds are usually not volatile, they would be expected to leave a residue, which in many cases, would be highly corrosive. Commercial extinguishing agents such as "Purple-K" and "Super-K," which are based on $KHCO_3$ and KCl, respectively, leave a sticky residue which is destructive to electronics and other delicate equipment. Toxicity is also a concern, particularly with heavy metals. The vapor pressure of $Fe(CO)_5$ is about 30 Torr, while $SnCl_4$ has a vapor pressure of about 20 Torr at ambient temperature. Thus, although relatively volatile, both compounds are highly toxic [139] and could not be deployed in the presence of people.

The high degree of activity exhibited by metallic flame inhibitors is the basis for their further consideration. In one study, Hayes and Kaskan determined that $NaHCO_3$ was 20 times more effective than CH_3Br, on a weight percent basis, in inhibiting premixed CH_4/air flames [192]. Milne, Green and Benson arrived at a similar conclusion regarding the relative effectiveness of alkali metals and the halons after studying inhibition of CH_4/air counterflow diffusion flames with CF_3Br and "Purple K" [103]. Three of the heavy metal compounds, $Fe(CO)_5$, CrO_2Cl_2 and $Pb(C_2H_5)_4$, are measurably more effective than the alkali metals and may be as much as two orders of magnitude more efficient than the halons in suppressing hydrocarbon flames [79,189]. Thus, it is conceivable that a solution containing a small amount of a metallic inhibitor dissolved in a volatile low toxicity solvent may result in a viable alternative to the halon extinguishing agents. Further elucidation of the operant principles of metallic flame inhibition will also serve to provide additional guidance in the search for halon replacements.

2. Past Flame Suppression Measurements

a. Alkali Metal Inhibitors

The fire suppression properties of alkali metal salts are well established. They are used as extinguishing agents in a wide variety of situations ranging from small household fires to large aircraft fuel fires. A large number of flame velocity and extinction measurements on these compounds have been reported in the literature [102,193,194,195,196,197,198,199,200,201].

The consensus which has developed on the basis of these experiments is that flame inhibition by the alkali metals is the result of a chemical, rather than a thermal process. The distinction between chemical and thermal suppression is clarified in Section II.B.4.b. Support for this hypothesis was obtained in early investigations of heptane and gasoline fires conducted by McCamy, Shroud and Lee [193] and independently by Lee and Robertson [194]. A major conclusion of both studies was that there was no correlation between heat capacity and fire suppression effectiveness of the alkali metal salts.

The effects of decomposition of the metallic extinguishing agents were not considered in these early studies and have yet to be fully resolved. Decomposition of alkali metal salts is a highly endothermic process and might be expected to facilitate suppression by reducing flame temperatures. This possibility was considered in a paper by Dodding, Simons and Stephens [195]. Their calculations indicated that the reduction in flame temperatures (at extinction) due to the presence of $NaHCO_3$, varied from about 35 to 75° C, depending on the average particle size of the powder. They went on to conclude that this was insufficient to account for the observed inhibition. Unfortunately, these results are open to interpretation. Ewing, Hughes and Carhart performed a similar analysis of the data for a wide variety of extinguishing agents, including some compounds of the alkali metals [116]. They arrived at just the opposite conclusion - that the data is consistent with thermal suppression, provided that the energy requirements for decomposition of the extinguishing agents are taken into account. At the present time, the chemical hypothesis seems to be more widely accepted. However, the alternative point of view, that the dominant mode of suppression is thermal in nature, cannot be dismissed out of hand. (See the discussion in Section II.B.4.b.)

The dependence of flame suppression effectiveness on particle size is an important concern because it has a critical impact on the design of efficient delivery systems. Dolan observed that the surface area of powders was a major factor in determining the ability of alkali metal salts to inhibit explosions in methane/air mixtures [196]. More recently, Birchall demonstrated that in some alkali metal salts, there is an optimal particle size for reduction in the velocities of town gas/air diffusion flames [197]. Birchall's explanation for this behavior was based on the argument that small particles will decompose before penetrating the flame front, whereas large particles will pass through before they can volatilize. In the same study, Birchall confirmed earlier observations reported by Friedrich [198] and by Lee and Robertson [194] that the oxalates of the alkali metals are particularly effective. It is now generally recognized that the order of effectiveness for a specified alkali metal is: oxalate > cyanate > carbonate > iodide > bromide > chloride > sulfate > phosphate, whereas the hierarchy for the metals is Rb > K > Na > Li [189].

The elucidation of the chemical mechanisms of alkali metal flame inhibition is a focal point of the research effort in this area. DeWitte, Vrebosch and van Tiggelen observed that alkali metal salts were incompletely volatilized in their downward burning $CH_4/(N_2 + O_2)$ premixed flames [199]. On this basis, they reasoned that the observed reduction in flame velocities was due to the recombination of combustion radicals on surfaces of the alkali metal particulates. Although a mechanism based on catalytic radical recombination seemed very likely, there was considerable debate over whether this occurs on particles (heterogeneous) or in the gas phase (homogeneous). Evidence supporting a homogeneous mechanism was obtained from measurements of temperature changes in Na-inhibited premixed CH_4/air flames by Iya, Wollowitz and Kaskan [200]. On the basis of spatially resolved concentration measurements, these researchers

TABLE 13. SILICON AND GERMANIUM FLAME INHIBITORS

Name	Formula	CASN	PHASE	Normal Boiling Point (nbp °C)	Vapor Pressure (atm) (298 K)	Heat Capacity (J/K-mole) (298 K)	Heat of Vaporization (kJ at nbp)
tetrachlorosilane	$SiCl_4$	10026-04-7	liquid	58	0.31	145	32
trichlorofluorosilane	$SiCl_3F$	14965-52-7	gas	15	1.46	92	26
tetrafluorosilane	SiF_4	7783-61-1	gas	-65	1510	74	22
bromotrifluorosilane	$SiBrF_3$	14049-39-9	gas	-42	10.5	$80^†$	18
tribromofluorosilane	$SiBr_3F$	18356-67-7	liquid	84	0.11	$150^†$	34
tetramethylsilane	$Si(CH_3)_4$	75-76-3	liquid	27	0.95	204	27
chlorotrimethylsilane	$Si(CH_3)_3Cl$	75-77-4	liquid	57	0.31	$175^†$	32
trichloromethylsilane	$Si(CH_3)Cl_3$	75-79-6	liquid	66	0.23	100	31
chloromethyltrimethylsilane	$Si(CH_3)_3CH_2Cl$	2344-80-1	liquid	98	na	$200^†$	na
tetrachlorogermane	$GeCl_4$	10038-98-9	liquid	83	0.11	$150^†$	35
tetramethylgermane	$Ge(CH_3)_4$	865-52-1	liquid	44	0.52	$200^†$	30

†Estimated for this report by authors
na = not available

were able to demonstrate that the degree of inhibition depended only on the concentration of Na atoms that had penetrated the reaction zone and was independent of initial particle size distribution and the nature of the ligand. This is compelling evidence in favor of a homogeneous mechanism as the efficiency of a heterogeneous catalyst would be expected to increase with the average size of the particles.

Further progress in determining the mechanism of alkali metal flame inhibition was made by Friedman and Levy [102]. They observed that the introduction of elemental potassium in the fuel stream of their counterflow diffusion burner had no effect on the strength of CH_4/air flames. (See the discussion of flame strength in Section II.B.3.e.) This observation could be cited in support of the thermal suppression mechanism discussed above. Thus, it may be argued that elemental potassium has no effect on flame speeds because it does not decompose (as do potassium salts) and, therefore, does not withdraw heat from the flame. Friedman and Levy, however, reasoned that this would also be expected if there was a critical intermediate that could not be produced from elemental potassium in sufficient concentrations to inhibit the flame. The results of thermochemical calculations suggested that KOH was a good possibility. Potassium salts, for example carbonates and oxalates, decompose by forming K_2O which readily reacts with H_2O to give KOH. Friedman and Levy attributed the failure of elemental potassium to inhibit the flame to the slow rate of conversion of K to KOH via the termolecular reaction $K + OH + X \rightarrow KOH + X$. The third body, X, is needed to dissipate the kinetic energy generated in the collision [202]. Independent results obtained by Iya, Wollowitz and Kaskan support the contention that this termolecular reaction is too slow to have a significant effect on the chemistry of alkali metal-inhibited flames [200]. Calculations made by these researchers using a kinetic model indicated that the reaction $Na + OH + X \rightarrow NaOH + X$ could not account for the observed OH concentration profiles. They went on to propose the alternative: $Na + H_2O \rightarrow Na\text{-}H_2O$; $Na\text{-}H_2O + OH \rightarrow H_2O + NaOH$. Although this mechanism removes the discrepancy between predicted and observed OH concentrations, it is inconsistent with Friedman and Levy's original observation that elemental K, and by implication the other alkali metals as well, is not an effective flame inhibitor.

The details of the mechanism of alkali metal flame inhibition, and in particular whether the catalysis is homogeneous or heterogenous, have not been fully resolved. Advocates of a homogeneous mechanism tend to agree that the critical intermediate is the alkali metal hydroxide (MOH). Flame inhibition is thought to result from removal of hydrogen radicals via the reaction $MOH + H \rightarrow M + H_2O$ [102,197,200,201]. Note that the inhibitor does not regenerate itself in this mechanism. It has been postulated, however, that a single functioning of each inhibitor molecule may be sufficient because of the low concentration of hydrogen radicals in hydrocarbon flames [102]. This mechanism also accounts for the surprising observation that halide salts are amongst the least effective alkali metal inhibitors [79,189]. The poisoning effect is due to the tendency of the halogen to tie-up the metal, thereby reducing the concentration of MOH in the flame.

b. Heavy Metal Inhibitors

Bulewicz and Padley demonstrated that low levels (ppm) of a wide range of metallic elements including Mg, Cr, Mn, Sn, U and Ba have a measurable effect on the recombination of hydrogen radicals in premixed $H_2/(O_2 + N_2)$ flames [203]. Despite this observation, which would appear to be good evidence that the ability to inhibit flames is widespread in metals, the data on metallic compounds which do not contain either Na or K is very limited.

A paper by Lask and Wagner appears to be the first serious attempt to investigate the influence of heavy metals on flames [79]. The effects of a wide range of additives on the flame velocities of premixed (stoichiometric) n-hexane flames were measured. These additives included $TiCl_4$, $SnCl_4$, $Fe(CO)_5$, $Pb(C_2H_5)_4$, CrO_2Cl_2, as well as a series of phosphorous and silicon compounds. The halogens, Br_2 and Cl_2, and halogenated hydrocarbons like CH_3Cl and CCl_4 were tested as well. An extended list which was compiled for a report [186] appears in a later paper by Morrison and Scheller [187]. Lask and Wagner reported that the flame inhibition exhibited by $Fe(CO)_5$, $Pb(C_2H_5)_4$ and CrO_2Cl_2 was at least an order of magnitude greater than what was observed with any of the other compounds that were tested. It required less than 0.02 percent (by volume) of these compounds in the fuel mixture to reduce the flame speed by 30 percent. The other two metallics, $TiCl_4$ and $SnCl_4$, were also effective requiring about 0.2 percent to achieve a 30 percent velocity reduction. For comparison, it took a mixture of 0.7 percent of Br_2 and almost 1.4 percent of CCl_4 to produce the same results.

The high degree of flame suppression activity exhibited by $Fe(CO)_5$ had been previously reported by Jost, Bonne and Wagner [204]. At the same time, it was noted that the catalytic efficiency depends on the concentration $Fe(CO)_5$ in the flame. This suggests that there may be two distinct mechanisms. A heterogeneous process may be operant at concentrations which exceed the saturation pressures of iron containing species (e. g. FeO) in the flame, whereas at lower concentrations of $Fe(CO)_5$ a homogeneous reaction predominates [205]. Hastie cites the observed fall-off in activity at higher concentrations as an indication that heterogeneous recombination may be less efficient [189].

There is, however, no direct evidence that any of these metallics exhibit homogeneous flame inhibition. Arguments for a heterogeneous mode have cited the streaky white appearance (indicative of the presence of nonvolatile oxides) and luminosity which are evident in transition metal inhibited flames [203]. It is known that $Fe(CO)_5$, in particular, produces finely divided oxides in flames [73,206]. In addition, particle temperatures in considerable excess of the adiabatic flame temperature (by as much as 400 k) have been observed [189,203]. This effect has been attributed to the heat released during surface recombination reactions [203,207,208]. Further evidence of heterogeneous inhibition was presented by Miller [209] and by Miller and Vree [210]. These investigators assigned continuum emission bands which were observed in low pressure methane flames (both diffusion and premixed) inhibited by $Fe(CO)_5$ and CrO_2Cl_2 to hot particles.

In a more recent study, Vanpee and Shirodkar examined the inhibition exhibited by a wide variety of metal chlorides, acetates and acetylacetonates using a counterflow diffusion burner with an ethanol/(air + N_2) flame [211]. After dissolving the compounds in ethanol, the solutions were atomized in a sonic nozzle and the resulting mist was mixed with the oxidizer. In all cases, with the exception of aluminum acetylacetonate, the solutions were effective inhibitors. The figure of merit was the increase in oxygen concentration in the oxidizer stream per unit concentration of the additive at extinction. The transition metal compounds were most effective when compared on a molar basis. However, when compared on a mass basis the alkali metal compounds were superior. Surprisingly, $Fe(CO)_5$ was rated comparatively low using either criterion.

3. Recommendations

Compounds of the alkali metals, as well as some heavy metals including Sn, Ti, Pb, Cr and Fe are flame inhibitors. Some of these compounds, for example $Fe(CO)_5$, $Pb(C_2H_5)_4$, CrO_2Cl_2, may be as much as two orders of magnitude more effective than the halons in inhibiting hydrocarbon flames. As is also the case with the halons, the dominant mechanism of metallic flame inhibition is thought to be chemical - involving the catalytic recombination of hydrogen and hydroxyl radicals, rather than thermal in nature. Although inconclusive, the evidence favors the hypothesis that the catalytic action of alkali metal inhibitors is homogeneous, whereas a heterogeneous mechanism appears to predominate in heavy metal inhibited flames. The efficiency of metallic inhibitors depends on the physical states and relative stabilities of the intermediates (for example metal oxides and hydroxides) which perform the catalytic function. Properties, such as volatility and average particle size, are also important because they determine the ability of the agent to penetrate the flame front.

An intensive search has not been successful in identifying low toxicity, high volatility, metallic flame inhibitors. The unfortunate conclusion is that pure metallic compounds are not acceptable halon replacements. This does not, however, preclude the possibility that a solution consisting of a small amount of a metallic inhibitor dissolved in a volatile solvent may make an effective fire extinguishing agent. The prospect of using $Fe(CO)_5$ as a fire suppression additive was first considered by Jost, Bonne and Wagner [204]. Mixtures consisting of halogenated fire inhibitors adsorbed on metal powders have also been examined [212].

A list of the metallic flame inhibitors recommended for further study is presented in Table 14 along with some of their relevant properties [190,191,213,214]. All of these chemicals, with the exception of $Pb(C_2H_5)_4$, are listed in the 1990 - 1991 Aldrich Catalogue. Many of these compounds, including the alkali metal acetates, $Fe(CO)_5$, and both potassium and chromium acetylacetonates, are soluble in ethanol. Flame inhibition measurements conducted by Vanpee and Shirodkar [211] suggest that these solutions might be effective as fire extinguishing agents. Additional experiments, involving solvents which are themselves flame inhibitors, are warranted.

K. INERT GASES

1. Justification for Consideration

In the present context, gases are considered to be inert if they do not undergo chemical transformation when they pass through a flame. As a result, these compounds can have no chemical effect on the flame chemistry and therefore must effect suppression by purely physical mechanisms. This point is discussed extensively in Section II-B. Comparitive studies involving inert and chemical agents should help to further elucidate the differences between physical and chemical suppression.

2. Past Flame Suppression Measurements

There are numerous flame inhibition and suppression investigations utilizing inert species. These will not be discussed in detail. Several were discussed in Section II.B. It should suffice to point out that CO_2 fire extinguishers are widely employed for local firefighting and that their effectiveness has been the subject of a great deal of investigation. Nitrogen has been proposed as an inerting agent [215,216,217] but has not been widely used. The third agent to be recommended here, argon, has not been tested as a practical firefighting agent.

3. Recommendations

The primary reason for including inert compounds on the list is to establish a baseline for purely physical fire suppression and to provide a basis for the comparison of chemical agents. It is recognized that these agents will not be suitable as replacements for all situations where the current commercial halons are used.

Three inert agents, N_2, CO_2, and Ar, have been chosen for inclusion on the list. These compounds are relatively inexpensive and have a range of heat capacities and densities. Table 15 summarizes the molecular properties of these three species.

As discussed in Section III.B.1 carbon tetrafluoride is also included on the list. This species is believed to be inert at flame temperatures and will thus provide an example of a still more complicated inert species for comparison purposes.

TABLE 14. METALLIC INHIBITORS

Name	Formula	CASN	PHASE	Normal Boiling Point (nbp °C)	Vapor Pressure (atm) (298 K)	Heat capacity (J/K-mol) (298 K)	Heat of vaporization (kJ at nbp)
sodium hydrogen carbonate	$NaHCO_3$	144-55-8	solid	decomposes	$0^{\dagger}$	88	na
sodium acetate	$NaC_2H_3O_2$	127-09-3	solid	decomposes	$0^{\dagger}$	80	na
potassium hydrogen carbonate	$KHCO_3$	298-14-6	solid	decomposes	$0^{\dagger}$	na	na
potassium oxalate	$K_2C_2O_4 \bullet H_2O$	6487-48-5	solid	decomposes	$0^{\dagger}$	na	na
potassium acetate	$K_2C_2H_3O_2$	127-08-2	solid	decomposes	$0^{\dagger}$	na	na
potassium acetylacetonate	$KC_5H_7O_2 \bullet \frac{1}{2}H_2O$	57402-46-7	solid	decomposes	na	na	na
chromium acetylacetonate	$Cr(C_5H_7O_2)_3$	21679-31-2	solid	340	na	na	na
chromyl chloride	CrO_2Cl_2	14977-61-8	liquid	116	0.024	na	41
tin (IV) chloride	$SnCl_4$	7646-78-8	liquid	114	0.030	165	37
titanium (IV) chloride	$TiCl_4$	7550-45-0	liquid	136	0.015	145	39
tetraethyl lead	$Pb(C_2H_5)_4$	78-00-2	liquid	≈ 200	0.00055	na	54
iron pentacarbonyl	$Fe(CO)_5$	13463-40-6	liquid	103	0.040	241	38

†Estimated for this report by authors
na = not available

TABLE 15. INERT GASES

Name	Formula	CASN	Phase	Normal boiling point (nbp °C)	Vapor pressure (atm) (298 K)	Heat capacity (J/K-mol) (298 K)	Heat of vaporization (kJ at nbp)
nitrogen	N_2	7727-37-9	gas	-195.8	na	29.3	5.6
carbon dioxide	CO_2	124-38-9	gas	-78.5(sub)	29.9	37.7	15.3
argon	Ar	7440-37-1	gas	-185.4	na	20.9	6.5

na = not available

SECTION IV

CONCLUSIONS AND RECOMMENDATIONS

A total of 103 compounds are included on the list which has been generated during the course of this study. Table 16 list the names of these compounds.

A quick review of these compounds reveals that a wide range of chemical families has been recommended for study. A more careful check reveals that the list meets the goals of the project by including species which are likely to be considered as immediate replacements for the current commercial halons, while at the same time, allowing the development of principles for fire suppression and ozone depletion which can be applied to a long-term search for replacements.

It is recommended that these compounds be tested in a very selective series of experimental investigations chosen to maximize the knowledge to be gained using the insights which have been used in the development of the list. For instance, certain halons are included on the list to characterize their behavior in the troposphere. Particular emphasis should be focused on whether or not these molecules will be attacked by OH radicals or undergo photolysis at wavelengths greater than 300 nm. The effects of changes in chemical structure on fire suppression and toxicity behavior must also be characterized. Similarly, compounds containing phosphorous and the metal compounds have been added to the list because literature reports indicate that these compounds are unusually effective fire suppressants. Efforts should be made to characterize the fire suppression effectiveness of these agents, and, if possible, characterize their mechanisms of chemical flame inhibition. Such insights will provide the knowledge base required for the intelligent design of alternative chemical fire suppressants.

The literature review performed as part of this investigation suggests that there has been no systematic search for new fire suppressants since the early 1950s. For this reason the review of the literature and recommendation of initial chemicals to investigate was a necessary and appropriate early step in the search for suitable alternatives. It is unlikely that this search will be easy, and the effort may not even lead to chemicals which are as effective and safe as the current commercial halons. On the other hand, the need for effective agents is so great that alternatives will be necessary for certain critical applications. The authors believe that this document will serve as the guidepost in the important effort to develop alternative chemicals for use in place of the current commercial halons.

TABLE 16. COMPLETE LIST OF RECOMMENDED COMPOUNDS

perfluoromethane
perfluoroethane
perfluoropropane
perfluoro-n-butane
perfluorocyclobutane
trifluoromethane
pentafluoroethane
1,1,1,2-tetrafluoroethane
dibromodifluoromethane
2,2-dibromo-1,1,1,2-tetrafluoroethane
chlorodifluoromethane
1,1,1-trichlorethane
2,2-dichloro-1,1,1-trifluoroethane
2-chloro-1,1,1,2-tetrafluoroethane
1,1-dichloro-1-fluoroethane
1-chloro-1,1-difluoroethane
bromodifluoromethane
bromochlorofluoromethane
2-bromo-2-chloro-1,1,1-trifluoroethane
2-bromo-1-chloro-1,2,2-trifluoroethane
1-bromo-1,1,2,2-tetrafluoroethane
2-bromo-1,1,1-trifluoroethane
1,2-dibromo-1,1,2-trifluoroethane
1,2-dibromo-1,1-difluoroethane
1,2-dibromo-1,2-difluoroethane
1-bromo-1,1,2,3,3,3-hexafluoropropane
1,3-dibromo-1,1,3,3-tetrafluoropropane
2,2-dibromo-1,1,3,3-tetrafluoropropane
1-bromo-1,1,3,3,3-pentafluoropropane
hexafluoracetone
trifluoroacetic anhydride
bis(perfluoroisopropyl) ketone
methyltrifluoroacetate
3-bromo-1,1,1-trifluoropropanone
bromopentafluoroacetone
bromomethyltrifluoroacetate
perfluoropropene
perfluorobutene-2
perfluorotoluene
1,1,3,3,3-pentafluoropropene-1
3,3,3 trifluoropropene
1,2-bis(perfluoro-n-butyl)ethylene
3-bromoperfluoropropene
1-bromoperfluoropropene
1,2-bis(perfluoromethyl)ethylene
1-bromoperfluoromethyl-2-perfluoromethylethylene
1-bromo-bis(perfluoromethyl)ethylene
tetris(perfluoromethyl)ethylene
tetrafluorodimethyl ether
pentafluorodimethyl ether
2-chloro-1-(difluoromethoxy)-1,1,2-trifluoroethane
isoflurane
perfluoro-2-butyltetrahydrofuran
bis(bromodifluoroethyl) ether
1-bromo-1,1,3,3,3-pentafluorodimethyl ether
bromoenflurane
octafluorofuran
3-bromoperfluorofuran
bis(perfluoromethyl) thioether
tris(perfluoromethyl) amine
iodotrifluoromethane
chlorodifluoroiodomethane
1-bromo-1,1,2,2-tetrafluoro-2-iodoethane
1,1,2,2-tetrafluoro-1,2-diiodoethane
iodomethane
iodoethane
1-iodopropane
1,1,1,2,2,3,3-heptafluoro-3-iodopropane
sulfur fluoride
sulfur chloride fluoride
sulfur bromide fluoride
phosphorous trifluoride
phosphorous trichloride
phosphorous bromide difluoride
phosphoryl fluoride
phosphoryl chloride
phosphoryl bromide fluoride
tetrachlorosilane
trichlorofluorosilane
tetrafluorosilane
bromotrifluorosilane
tribromofluorosilane
tetramethylsilane
chlorotrimethylsilane
trichloromethylsilane
chloromethyltrimethylsilane
tetrachlorogermane
tetramethylgermane
sodium hydrogen carbonate
sodium acetate
potassium hydrogen carbonate
potassium oxalate
potassium acetate
potassium acetylacetonate
chromium acetylacetonate
chromyl chloride
tin (IV) chloride
titanium (IV) chloride
tetraethyl lead
iron pentacarbonyl
nitrogen
carbon dioxide
argon

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APPENDIX A

DATA SHEETS FOR SELECTED COMPOUNDS

This Appendix contains data sheets for each of the selected compounds that include formulae, common names, classification numbers, physical properties, commercial sources and prices (if available), toxicity information, references to fire suppression results, and additional relevant comments.

Name: perfluoromethane

Compound group: Halogenated hydrocarbons
Formula: CF_4
Alternate Names: halon 14, cfc 14

CASN: 75-73-0
Normal boiling point (nbp °C): -128
Vapor pressure (atm at 298 K): Pressure greater than critical pressure.
Heat capacity (J/K-mol at 298 K): 61
Heat of Vaporization (kJ/mol at nbp): 11.6
Source: PCR, Inc., Gainesville, FL 32602, (800)-331-6313
Price: $65/50g

Toxicity: Essentially non-toxic. CF_4 can be view as a simple asphyxiant, that is its action is only to replace air.

Comments: There is a substantial body of evidence to indicate the effectiveness of CF_4; however, it will require a much larger concentration than halon 1301 and it may be a significant greenhouse gas.

Fire suppression studies:

Ewing, C.T., Hughes, J.T. and Carhart, H.W., "The Extinction of Hydrocarbon Flames based on the Heat-absorption Processes which Occur in them," Fire and Materials, vol. 8, pp 148-156, 1984.

McHale, E.T., "Survey of Vapor Phase Chemical Agents for Combustion Suppression," Fire Research Abstracts and Reviews, vol. 11, pp 90-104, 1969.

Name: perfluoroethane

Compound group:	Halogenated hydrocarbons
Formula:	C_2F_6
Alternate Names:	halon 26, cfc 116

CASN:	76-16-4
Normal boiling point (nbp °C):	-78
Vapor pressure (atm at 298 K):	Pressure greater than critical pressure.
Heat capacity (J/K-mol at 298 K):	106
Heat of Vaporization (kJ/mol at nbp):	16.1
Source:	PCR,Inc., Gainesville,FL 32602, (800)-331-6313
Price:	$40/100g

Toxicity: Very low, also primarily an asphyxiant.

Comments: A more effective fire suppressant than CF_4, less effective than C_3F_8, also possible problems with greenhouse effect.

Fire suppression studies:

McHale,E.T., "Survey of Vapor Phase Chemical Agents for Combustion Suppression," Fire Research Abstracts and Reviews, vol. 11, pp 90-104, 1969.

Name: perfluoropropane

Compound group:	Halogenated hydrocarbons
Formula:	C_3F_8
Alternate Names:	halon 38, cfc 218

CASN:	76-19-7
Normal boiling point (nbp °C):	-36
Vapor pressure (atm at 298 K):	8.69
Heat capacity (J/K-mol at 298 K):	148
Heat of Vaporization (kJ/mol at nbp):	19.7
Source:	PCR, Inc., Gainesville, FL 32602, (800)-331-6313
Price:	$75/50g

Toxicity: Sax and Lewis give inhalation data for rats and mice. Rated as mildly toxic by inhalation.

Sax, N.I.; Lewis, R.J.; "Dangerous Properties of Industrial Materials," Van Norstrand Reinhold, New York (1987).

Comments: This compound has the right range for physical properties for a replacement for halon 1301. As with the other perfluorinated compounds it is likely to be a problem as greenhouse gas.

Name: perfluoro-n-butane

Compound group:	Halogenated hydrocarbons
Formula:	C_4F_{10}
Alternate Names:	Outside of halon naming conventions.

CASN:	355-25-9
Normal boiling point (nbp °C):	-2
Vapor pressure (atm at 298 K):	2.63
Heat capacity (J/K-mol at 298 K):	189
Heat of Vaporization (kJ/mol at nbp):	23.2
Source:	PCR, Inc., Gainesville, FL 32602, (800)-331-6313
Price:	$50/25g

Toxicity: As the perfluorinated saturated hydrocarbons become larger, there are increasing toxicity concerns. There has been very limited long term study of these compounds.

Comments:

Previous fire suppression studies:

McHale, E.T., "Survey of Vapor Phase Chemical Agents for Combustion Suppression," Fire Research Abstracts and Reviews, vol. 11, pp 90-104, 1969.

Name: perfluorocyclobutane

Compound group:	Halogenated hydrocarbons
Formula:	C_4F_8
Alternate Names:	
CASN:	115-25-3
Normal boiling point (nbp °C):	-6
Vapor pressure (atm at 298 K):	3.07
Heat capacity (J/K-mol at 298 K):	156
Heat of Vaporization (kJ/mol at nbp):	23.0
Source:	PCR, Inc., Gainesville, FL 32602, (800)-331-6313
Price:	$75/25g

Toxicity: Toxicity suspect. Decomposition products may be exceptionally toxic. There is some anecdotal evidence that this compound will decompose in a flame or on hot surfaces to produce perfluoroisobutene which is very toxic. This report does not attempt to cover combustion product toxicity, but the toxicity of the perfluoroisobutene has been reported to be so high that some caution needs to be advised with regard to this compound. Sax and Lewis give only limited data to indicated low direct toxicity.

Sax, N.I.; Lewis, R.J.; "Dangerous Properties of Industrial Materials," Van Norstrand Reinhold, New York (1987).

Comments: Except for its toxic effects, this compound would be an interesting candidate for the investigation of chemical energy absorption since it breaks down into two C_2F_4 molecules in the gas phase.

Fire suppression studies:

McHale, E.T., "Survey of Vapor Phase Chemical Agents for Combustion Suppression," Fire Research Abstracts and Reviews, vol. 11, pp 90-104, 1969.

Name: trifluoromethane

Compound group:	Halogenated hydrocarbons
Formula:	CHF_3
Alternate Names:	halon 13, cfc 23

CASN:	75-46-7
Normal boiling point (nbp °C):	-82
Vapor pressure (atm at 298 K):	46.7
Heat capacity (J/K-mol at 298 K):	51
Heat of Vaporization (kJ/mol at nbp):	16.7
Source:	Aldrich Chemical, Milwaukee, WI 53201, (800)-558-9160
Price:	$120/200g

Toxicity: Toxicity is expected to be very low. Clayton has reported data showing no fatalities in a 2 hour exposure of guinea pigs at 20% trifluoromethane.

Clayton, J.W., "Fluorocarbon Toxicity and Biological Action," Fluorine Chemistry Reviews (ed. Tarrant, P.), vol. 1, 197-252, 1967.

Comments: This compound is undergoing tests as an alternative cfc for uses other than fire suppression.

Fire suppression studies:

McHale, E.T., "Survey of Vapor Phase Chemical Agents for Combustion Suppression," Fire Research Abstracts and Reviews, vol. 11, pp 90-104, 1969.

Name: pentafluoroethane

Compound group: Halogenated hydrocarbons
Formula: C_2HF_5
Alternate Names: halon 25, cfc 125

CASN: 354-33-6
Normal boiling point (nbp °C): -48.5
Vapor pressure (atm at 298 K): 10[†]
Heat capacity (J/K-mol at 298 K): 94
Heat of Vaporization (kJ/mol at nbp): 20[†]
Source: PCR, Inc., Gainesville, FL 32602, (800)-331-6313
Price: $120/50g

Toxicity: DuPont has given a value for toxicity of >>100,000 ppm for rats exposed for 4 hrs. In the same note the stated toxicity of CF_3Br was 400,000 - 800,000 ppm. This data comes from Clayton who reports essentially the same value (Clayton was at Haskell Labs - a branch of DuPont).

Clayton, J.W., "Fluorocarbon Toxicity and Biological Action," Fluorine Chemistry Reviews (ed. Tarrant, P.), vol. 1, 197-252, 1967.

Comments: This compound is undergoing tests as an alternative cfc for uses other than fire suppression. In addition DuPont has recently announced that it will be making C_2HF_5 available for testing as a fire suppressant.

[†] Estimated for this report by authors.

Name: 1,1,1,2-tetrafluoroethane

Compound group:	Halogenated hydrocarbons
Formula:	$C_2H_2F_4$
Alternate names:	halon 24, cfc 134

CASN:	881-97-72
Normal boiling point (nbp °C):	-26.5
Vapor pressure (atm at 298 K):	$7^{\dagger}$
Heat capacity (J/K-mol at 298 K):	$87^{\dagger}$
Heat of Vaporization (kJ/mol at nbp):	$22^{\dagger}$
Source:	PCR, Inc., Gainesville, FL 32602, (800)-331-6313
Price:	$195/100g

Toxicity: Data was not found for this compound, but the 1,1,1 trifluoroethane was reported to have anesthetic dose for 50% of the mice tested of 50-60% and no fatal dose was reported. In general the more highly fluorine substituted the molecule, the lower its toxicity, so that this compound would be expected to be at least as safe as the 1,1,1 trifluoro compound.

Robbins, B.H., "Preliminary studies of the anesthetic activity of fluorinated hydrocarbons," J. Pharmacology & Experimental Therapeutics, vol. 86, pp 197-204, 1946.

Comments: This compound is undergoing tests as an alternative cfc for uses other than fire suppression. Note that only compounds with small numbers of H atoms were considered among the alternative cfc's. As the number of H atoms increases and the corresponding halogen content of the molecule decreases, the fire suppression effectiveness of the molecule will decline.

† Estimated for this report by authors.

Name: dibromodifluoromethane

Compound group:	Halogenated hydrocarbons
Formula:	CBr_2F_2
Alternate Names:	halon 1202, cfc 12B2

CASN:	75-61-6
Normal boiling point (nbp °C):	-58
Vapor pressure (atm at 298 K):	15.8
Heat capacity (J/K-mol at 298 K):	69
Heat of Vaporization (kJ/mol at nbp):	17.5
Source:	PCR, Inc., Gainesville, FL 32602, (800)-331-6313
Price:	$35/100g

Toxicity: Clayton reports LC50 in rats of 5.5% for a 15 min exposure.

Clayton, J.W., "Fluorocarbon Toxicity and Biological Action," Fluorine Chemistry Reviews (ed. Tarrant, P.), vol. 1, 197-252, 1967.

Comments: This compound will probably be destroyed by solar photolysis in the troposphere.

Fire suppression studies:

Ewing, C.T., Hughes, J.T. and Carhart, H.W., "The Extinction of Hydrocarbon Flames based on the Heat-absorption Processes which Occur in them," Fire and Materials, vol. 8, pp 148-156, 1984.

McHale, E.T., "Survey of Vapor Phase Chemical Agents for Combustion Suppression," Fire Research Abstracts and Reviews, vol. 11, pp 90-104, 1969.

NAME: 2,2-dibromo-1,1,1,2-tetrafluoroethane

Compound group:	Halogenated hydrocarbons
Formula:	$C_2Br_2F_4$
Alternate Names:	1,1 dibromotetrafluoroethane, FC-114aB2

CASN:	27336-28-8
Normal boiling point (nbp °C):	50[†]
Vapor pressure (atm at 298 K):	0.4[†]
Heat capacity (J/K-mol at 298 K):	116[†]
Heat of Vaporization (kJ/mol at nbp):	29[†]
Source:	PCR,Inc., Gainesville,FL 32602, (800)-331-6313
Price:	$160/100g

Toxicity: No data found. This is probably more toxic than the symmetric analog since it is less stable.

Comments: This compound is the asymmetric form of halon 2402, and as such could also be called halon 2402, to avoid confusion this name is not used. Because of the two bromine atoms on a single carbon, this compound should be very sensitive to solar photolysis in the troposphere.

[†] Estimated for this report by authors.

Name: chlorodifluoromethane

Compound group:	Halogenated hydrocarbons
Formula:	$CHClF_2$
Alternate Names:	halon 121, cfc 22

CASN:	75-45-6
Normal boiling point (nbp °C):	-41
Vapor pressure (atm at 298 K):	10.1
Heat capacity (J/K-mol at 298 K):	57
Heat of Vaporization (kJ/mol at nbp):	20.2
Source:	Aldrich Chemical, Milwaukee, WI 53201, (800)-558-9160
Price:	$30/100g

Toxicity: This compound has been tested as an anesthetic and the reported AD50 (the dose at which 50% of the test animals are anesthetized) is 20%. No data on fatality was found.

Davies, R.H., Bagnall, R.D., Jones, W.G.M., "A Quantitative Interpretation of Phase Effects in Anaesthesia," Int. J. Quantum Chem: Quantum Biology Symp. No. 1, pp 201-212, 1974.

Comments: This compound is undergoing tests as an alternative cfc for uses other than fire suppression.

Name: 1,1,1-trichloroethane

Compound group:	Halogenated hydrocarbons
Formula:	$C_2H_3Cl_3$
Alternate Names:	halon 203, cfc 14

CASN:	71-55-6
Normal boiling point (nbp °C):	74
Vapor pressure (atm at 298 K):	0.16
Heat capacity (J/K-mol at 298 K):	93
Heat of Vaporization (kJ/mol at nbp):	29.8
Source:	Aldrich Chemical, Milwaukee, WI 53201, (800)-558-9160
Price:	$8/100ml

Toxicity: Sax and Lewis give extensive data and conclude that the compound is moderately toxic by inhalation. In addition it is an experimental teratogen and sensitizes the heart. Lowest effective concentration in humans for an effect on central nervous system is reported at 200ppm over a 4H exposure.

Sax, N.I.; Lewis, R.J.; "Dangerous Properties of Industrial Materials," Van Norstrand Reinhold, New York (1987).

Comments: This compound is undergoing tests as an alternative cfc for uses other than fire suppression.

Name: 2,2-dichloro-1,1,1-trifluoroethane

Compound group:	Halogenated hydrocarbons
Formula:	$C_2HCl_2F_3$
Alternate Names:	halon 2302, cfc 123

CASN:	306-83-2
Normal boiling point (nbp °C):	24
Vapor pressure (atm at 298 K):	1†
Heat capacity (J/K-mol at 298 K):	102
Heat of Vaporization (kJ/mol at nbp):	26†
Source:	PCR, Inc., Gainesville, FL 32602, (800)-331-6313
Price:	$75/1kg

Toxicity: Sax and Lewis report 14% in 4 min for mouse toxicity. Robbins reports an LD50 of 7.7%. Both Robbins and Davies et al. report AD50 of about 2.5%.

Sax, N.I.; Lewis, R.J.; "Dangerous Properties of Industrial Materials," Van Norstrand Reinhold, New York (1987).

Robbins, B.H., "Preliminary studies of the anesthetic activity of fluorinated hydrocarbons," J. Pharmacology & Experimental Therapeutics, vol. 86, pp 197-204, 1946.

Davies, R.H., Bagnall, R.D., Jones, W.G.M., "A Quantitative Interpretation of Phase Effects in Anaesthesia," Int. J. Quantum Chem: Quantum Biology Symp. No. 1, pp 201-212, 1974.

Comments: This compound is undergoing tests as an alternative cfc for uses other than fire suppression.

† Estimated for this report by authors.

Name: 2-chloro-1,1,1,2-tetrafluoroethane

Compound group: Halogenated hydrocarbons
Formula: C_2HClF_4
Alternate Names: halon 241

CASN: 2837-89-0
Normal boiling point (nbp °C): -12
Vapor pressure (atm at 298 K): 4[†]
Heat capacity (J/K-mol at 298 K): 101[†]
Heat of Vaporization (kJ/mol at nbp): 23[†]
Source: PCR, Inc., Gainesville, FL 32602, (800)-331-6313
Price: $48/100g

Toxicity: Davies et al. report an AD50 of 15% in mice.

Davies, R.H., Bagnall, R.D., Jones, W.G.M., "A Quantitative Interpretation of Phase Effects in Anaesthesia," Int. J. Quantum Chem: Quantum Biology Symp. No. 1, pp 201-212, 1974.

Comments: This compound is undergoing tests as an alternative cfc for uses other than fire suppression.

[†] Estimated for this report by authors.

Name: 1,1-dichloro-1-fluoroethane

Compound group:	Halogenated hydrocarbons
Formula:	$C_2H_3Cl_2F$
Alternate Names:	halon 212

CASN:	1717-00-6
Normal boiling point (nbp °C):	32
Vapor pressure (atm at 298 K):	0.5†
Heat capacity (J/K-mol at 298 K):	89†
Heat of Vaporization (kJ/mol at nbp):	27†
Source:	PCR, Inc., Gainesville, FL 32602, (800)-331-6313
Price:	$65/250g

Toxicity: Robbins reports an AD50 of 2.5% and an LD50 of 5% in mice. Davies et al. report an AD50 of 6% in mice.

Robbins, B.H., "Preliminary studies of the anesthetic activity of fluorinated hydrocarbons," J. Pharmacology & Experimental Therapeutics, vol. 86, pp 197-204, 1946.

Davies, R.H., Bagnall, R.D., Jones, W.G.M., "A Quantitative Interpretation of Phase Effects in Anaesthesia," Int. J. Quantum Chem: Quantum Biology Symp. No. 1, pp 201-212, 1974.

Comments: This compound is undergoing tests as an alternative cfc for uses other than fire suppression.

† Estimated for this report by authors.

Name: 1-chloro-1,1-difluoroethane

Compound group:	Halogenated hydrocarbons
Formula:	$C_2H_3ClF_2$
Alternate Names:	halon 221

CASN:	75-68-3
Normal boiling point (nbp °C):	-10
Vapor pressure (atm at 298 K):	3.33
Heat capacity (J/K-mol at 298 K):	82
Heat of Vaporization (kJ/mol at nbp):	22.4
Source:	Aldrich Chemical, Milwaukee, WI 53201, (800)-558-9160
Price:	$40/100g

Toxicity: Davies et al. report AD50 of 23% for mice, Robbins[2] reported AD50 of 25% and no fatalities.

Davies, R.H., Bagnall, R.D., Jones, W.G.M., "A Quantitative Interpretation of Phase Effects in Anaesthesia," Int. J. Quantum Chem: Quantum Biology Symp. No. 1, pp 201-212, 1974.

Robbins, B.H., "Preliminary studies of the anesthetic activity of fluorinated hydrocarbons," J. Pharmacology & Experimental Therapeutics, vol. 86, pp 197-204, 1946.

Comments: This compound is undergoing tests as an alternative cfc for uses other than fire suppression.

Name: bromodifluoromethane

Compound group:	Halogenated hydrocarbons
Formula:	$CHBrF_2$
Alternate Names:	halon 1201

CASN:	1151-62-2
Normal boiling point (nbp °C):	-15
Vapor pressure (atm at 298 K):	4.4
Heat capacity (J/K-mol at 298 K):	59
Heat of Vaporization (kJ/mol at nbp):	23†
Source:	Great Lakes Chemicals will be selling this in the near future.
Price:	na

Toxicity: Toxicity, as reported by Great Lakes Chemicals, is greater than halon 1211 and much greater that halon 1301. Cardiac sensitization not reported.

Comments: Great Lakes Chemicals has recently announced that they will be making this compound available as a commercial fire suppressant.

Fire suppression studies:

McHale, E.T., "Survey of Vapor Phase Chemical Agents for Combustion Suppression," Fire Research Abstracts and Reviews, vol. 11, pp 90-104, 1969.

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† Estimated for this report by authors, na = not available.

Name: bromochlorofluoromethane

Compound group:	Halogenated hydrocarbons
Formula:	CHBrClF
Alternate Names:	halon 1111

CASN:	593-98-6
Normal boiling point (nbp °C):	36
Vapor pressure (atm at 298 K):	0.5[†]
Heat capacity (J/K-mol at 298 K):	63
Heat of Vaporization (kJ/mol at nbp):	28[†]
Source:	No commercial source was identified
Price:	na

Toxicity: Davies et al. report an AD50 of 1% for mice. This compound may be expected to be substantially more toxic than many of the other halons.

Davies, R.H., Bagnall, R.D., Jones, W.G.M., "A Quantitative Interpretation of Phase Effects in Anaesthesia," Int. J. Quantum Chem: Quantum Biology Symp. No. 1, pp 201-212, 1974.

Comments: This compound will have a relatively short lifetime due to solar photolysis as well as reacting with OH.

[†] Estimated for this report by authors, na = not available.

Name: 2-bromo-2-chloro-1,1,1-trifluoroethane

Compound group:	Halogenated hydrocarbons
Formula:	$C_2HBrClF_3$
Alternate Names:	halothane, narcotane

CASN:	151-67-7
Normal boiling point (nbp °C):	50
Vapor pressure (atm at 298 K):	0.4
Heat capacity (J/K-mol at 298 K):	104
Heat of Vaporization (kJ/mol at nbp):	27.3
Source:	PCR, Inc., Gainesville, FL 32602, (800)-331-6313
Price:	$25/100g

Toxicity: Sax and Lewis give extensive data on this molecule since it is widely used as an anaesthetic. Human toxicity over 3-hour periods starts to occur at about 7000 ppm. In addition it is a sever eye irritant which may make it undesirable as a suppressant where continued occupation of the site is necessary. Davies et al. report AD50 in mice of less than 1%, Robbins does not report data on this compound but has data on the 2-bromo-1-chloro-1,1-difluoro ethane and gives AD50 of 0.8% and LD50 of 3.7%.

Sax, N.I.; Lewis, R.J.; "Dangerous Properties of Industrial Materials," Van Norstrand Reinhold, New York (1987).

Davies, R.H., Bagnall, R.D., Jones, W.G.M., "A Quantitative Interpretation of Phase Effects in Anaesthesia," Int. J. Quantum Chem: Quantum Biology Symp. No. 1, pp 201-212, 1974.

Robbins, B.H., "Preliminary studies of the anesthetic activity of fluorinated hydrocarbons," J. Pharmacology & Experimental Therapeutics, vol. 86, pp 197-204, 1946.

Comments: This compound is included as a research topic. As an anaesthetic it is not appropriate as a general fire suppressant but it represents an important class of compounds that can undergo HBr elimination.

Name: 2-bromo-1-chloro-1,2,2-trifluoroethane

Compound group:	Halogenated hydrocarbons
Formula:	$C_2HBrClF_3$
Alternate Names:	

CASN:	354-06-3
Normal boiling point (nbp °C):	53
Vapor pressure (atm at 298 K):	0.4†
Heat capacity (J/K-mol at 298 K):	103
Heat of Vaporization (kJ/mol at nbp):	29†
Source:	PCR, Inc., Gainesville, FL 32602, (800)-331-6313
Price:	$25/100g

Toxicity: Sax and Lewis give data for mice. Lowest toxic concentration reported is 35 ppt over 17 minutes. Davies et al. give an AD50 of 1.1% for mice.

Sax, N.I.; Lewis, R.J.; "Dangerous Properties of Industrial Materials," Van Norstrand Reinhold, New York (1987).

Davies, R.H., Bagnall, R.D., Jones, W.G.M., "A Quantitative Interpretation of Phase Effects in Anaesthesia," Int. J. Quantum Chem: Quantum Biology Symp. No. 1, pp 201-212, 1974.

Comments: This compound is more interesting from the point of view of undergoing HBr elimination since the H and Br are on adjacent carbon atoms rather than on the same carbon atom.

† Estimated for this report by authors.

Name: 1-bromo-1,1,2,2-tetrafluoroethane

Compound group: Halogenated hydrocarbons
Formula: C_2HBrF4
Alternate Names: halon 2401

CASN: 354-07-4
Normal boiling point (nbp °C): -5
Vapor pressure (atm at 298 K): 3.1
Heat capacity (J/K-mol at 298 K): 86[†]
Heat of Vaporization (kJ/mol at nbp): 23.8
Source: No commercial sources identified.
Price: R. Du Boisson of PRC states that this should be easy to make but start up costs alone will make the cost in the range of $2000+ (amount does not matter greatly)

Toxicity: Davies et al. give an AD50 of 7%. Based on the average value of the AD50/LD50 observed for bromo-fluoro compounds the LD50 might be estimated to be in the range of 20%.

Davies, R.H., Bagnall, R.D., Jones, W.G.M., "A Quantitative Interpretation of Phase Effects in Anaesthesia," Int. J. Quantum Chem: Quantum Biology Symp. No. 1, pp 201-212, 1974.

Comments: This is the most ideal candidate for undergoing HBr elimination. The resulting perfluoroethene is not stable and would probably take up radicals in the flame adding to its effectiveness. This molecule should be given high priority in testing and is a strong candidate for fundamental research since data on the elimination reaction does not exist and estimation techniques for this class of reactions are not very accurate. The relatively low toxicity also makes this a strong candidate.

[†] Estimated for this report by authors.

Name: 2-bromo-1,1,1-trifluoroethane

Compound group: Halogenated hydrocarbons
Formula: $C_2H_2BrF_3$
Alternate Names:

CASN: 421-06-7
Normal boiling point (nbp °C): 26
Vapor pressure (atm at 298 K): 1[†]
Heat capacity (J/K-mol at 298 K): 91[†]
Heat of Vaporization (kJ/mol at nbp): 27[†]
Source: Aldrich Chemical, Milwaukee, WI 53201, (800)-558-9160
Price: $28/25g

Toxicity: Robbins reports AD50 of 2.8% and LD50 of 11.7%

Robbins, B.H., "Preliminary studies of the anesthetic activity of fluorinated hydrocarbons," J. Pharmacology & Experimental Therapeutics, vol. 86, pp 197-204, 1946.

Comments: See comments on previous molecule. Increasing the fluorine content raised the AD50 from 2.8% in this molecule to 7% in the previous molecule. These small differences in the molecules may change the toxicity a great deal and possibly only marginally affect the fire suppression. Note that in this case the increase in F atom content would be expected to increase the fire suppression.

[†] Estimated for this report by authors.

Name: 1,2-dibromo-1,1,2-trifluoroethane

Compound group:	Halogenated hydrocarbons
Formula:	$C_2HBr_2F_3$
Alternate Names:	
CASN:	354-04-1
Normal boiling point (nbp °C):	76
Vapor pressure (atm at 298 K):	0.2†
Heat capacity (J/K-mol at 298 K):	106†
Heat of Vaporization (kJ/mol at nbp):	31†
Source:	PCR, Inc., Gainesville, FL 32602, (800)-331-6313
Price:	$145/250g

Toxicity: Davies et al. report AD50 of 0.6%, so that this molecule must be considered more toxic than most in the halogenated hydrocarbon group.

Davies, R.H., Bagnall, R.D., Jones, W.G.M., "A Quantitative Interpretation of Phase Effects in Anaesthesia," Int. J. Quantum Chem: Quantum Biology Symp. No. 1, pp 201-212, 1974.

Comments: Also a candidate for HBr elimination. Vapor pressure may be too low for many applications, but in adverse environments where wind shear of the suppressant stream is a factor, compounds with higher boiling points and therefore greater resistance to dispersion of the stream may be advantageous.

† Estimated for this report by authors.

Name: 1,2-dibromo-1,1-difluoroethane

Compound group:	Halogenated hydrocarbons
Formula:	$C_2H_2Br_2F_2$
Alternate Names:	

CASN:	75-82-1
Normal boiling point (nbp °C):	93
Vapor pressure (atm at 298 K):	0.1†
Heat capacity (J/K-mol at 298 K):	95†
Heat of Vaporization (kJ/mol at nbp):	33†
Source:	PCR, Inc., Gainesville, FL 32602, (800)-331-6313
Price:	$25/100g

Toxicity: Sax and Lewis rate this as mildly toxic by inhalation. Data given indicate toxicity in rats at the 5 ppt level for long exposure.

Sax, N.I.; Lewis, R.J.; "Dangerous Properties of Industrial Materials," Van Norstrand Reinhold, New York (1987).

Comments: May also eliminate HBr. Boiling point is very high.

† Estimated for this report by authors.

Name: 1,2-dibromo-1,2-difluoroethane

Compound group:	Halogenated hydrocarbons
Formula:	$C_2H_2Br_2F_2$
Alternate Names:	halon 2202
CASN:	20705-29-7
Normal boiling point (nbp °C):	102[†]
Vapor pressure (atm at 298 K):	0.06[†]
Heat capacity (J/K-mol at 298 K):	97[†]
Heat of Vaporization (kJ/mol at nbp):	33[†]
Source:	R. Du Boisson of PRC indicated that this compound is very difficult to make.
Price:	na
Toxicity:	
Comments:	

[†] Estimated for this report by authors, na = not available.

Name: 1-bromo-1,1,2,3,3,3-hexafluoropropane

Compound group:	Halogenated hydrocarbons
Formula:	C_3HBrF_6
Alternate Names:	

CASN:	2252-78-0
Normal boiling point (nbp °C):	35.5
Vapor pressure (atm at 298 K):	0.5†
Heat capacity (J/K-mol at 298 K):	145†
Heat of Vaporization (kJ/mol at nbp):	29†
Source:	PCR, Inc., Gainesville, FL 32602, (800)-331-6313
Price:	$85/100g

Toxicity: Sax and Lewis have data on a related compound 3-bromo-1,1,2,2-tetrafluoropropane (CASN 679-84-5) : human lowest toxic concentration was given as 40 ppt. Generally increasing the fluorine content at the expense of the hydrogen reduces toxicity so this compound may be expected to be less toxic. Davies et al. report an AD50 of <2% for the 1-bromo-1,1,3,3,3-pentafluoro compound. Again, increasing the fluorine content should increase the safety of the compound. The data does seem to indicate that for the larger halocarbons the ratio of AD50 to LD50 is lower, but the data are not conclusive.

Sax, N.I.; Lewis, R.J.; "Dangerous Properties of Industrial Materials," Van Norstrand Reinhold, New York (1987).

Davies, R.H., Bagnall, R.D., Jones, W.G.M., "A Quantitative Interpretation of Phase Effects in Anaesthesia," Int. J. Quantum Chem: Quantum Biology Symp. No. 1, pp 201-212, 1974.

Comments: This compound is one of the test cases for the HBr elimination.

† Estimated for this report by authors.

Name: 1,3-dibromo-1,1,3,3-tetrafluoropropane

Compound group:	Halogenated hydrocarbons
Formula:	$C_3H_2Br_2F_4$
Alternate Names:	
CASN:	460-86-6
Normal boiling point (nbp °C):	118[†]
Vapor pressure (atm at 298 K):	0.04[†]
Heat capacity (J/K-mol at 298 K):	138[†]
Heat of Vaporization (kJ/mol at nbp):	35[†]
Source:	No commercial source was identified
Price:	na

Toxicity: Toxicity probably much greater that the 1-bromo-hexafluoropropane discussed above.

Comments: Vapor pressure probably eliminates this compound as a practical suppressant, but it is included as an example of the propanes which may be capable of delivering much higher heat capacities.

[†] Estimated for this report by authors, na = not available.

Name: 2,2-dibromo-1,1,3,3-tetrafluoropropane

Compound group: Halogenated hydrocarbons
Formula: $C_3H_2Br_2F_4$
Alternate Names:

CASN: na
Normal boiling point (nbp °C): 120[†]
Vapor pressure (atm at 298 K): 0.03[†]
Heat capacity (J/K-mol at 298 K): 137[†]
Heat of Vaporization (kJ/mol at nbp): 35[†]
Source: No commercial source was identified
Price: na

Toxicity: Probably greater than 1-bromo-hexafluoro propane discussed above.

Comments:

[†] Estimated for this report by authors, na = not available.

Name: 1-bromo-1,1,3,3,3-pentafluoropropane

Compound group:	Halogenated hydrocarbons
Formula:	$C_3H_2BrF_5$
Alternate Names:	
CASN:	460-88-8
Normal boiling point (nbp °C):	51[†]
Vapor pressure (atm at 298 K):	0.4[†]
Heat capacity (J/K-mol at 298 K):	133[†]
Heat of Vaporization (kJ/mol at nbp):	29[†]
Source:	No commercial source was identified
Price:	na

Toxicity: Probably greater than the 1-bromo-hexafluoro propane discussed above.

Comments:

[†] Estimated for this report by authors, na = not available.

Name: hexafluoracetone

Compound group:	Halogenated Ketones, Anhydrides and Esters
Formula:	CF_3COCF_3
Alternate Names:	

CASN:	684-16-2
Normal boiling (nbp °C):	-26
Vapor pressure (atm at 298 K):	6.65
Heat capacity at (J/K-mol at 298 K):	118
Heat of Vaporization (kJ/mol at nbp):	20.9
Source:	PCR Incorporated, Gainesville, FL 32602 800-331-6313
Price:	$175.00/100g

Toxicity: Hexafluoroacetone is given a hazard rating of 3 in Sax and Lewis.

Sax, N. I., and Lewis, R. J. Dangerous Properties of Industrial Materials 7th Edition, Van Nostrand Reinhold, 1989

Comments: A detailed description of the physics and chemistry of hexafluoroacetone can be found in a review by Krespan and Middleton

Krespan, C. G. and Middleton, W. J., "Hexafluoroacetone" in Fluorine Chemistry Reviews, 1, 145-196, 1967

Name: trifluoroacetic anhydride

Compound group:	Halogenated Ketones, Anhydrides and Esters
Formula:	$CF_3COOCOCF_3$
Alternate Names:	

CASN:	407-25-0
Normal boiling (nbp °C):	40
Vapor pressure (atm at 298 K):	.4†
Heat capacity at (J/K-mol at 298 K):	155†
Heat of Vaporization (kJ/mol at nbp):	28†
Source:	PCR Incorporated, Gainesville, FL 32602 800-331-6313
Price:	$125.00/1kg

Toxicity: Trifluoroacetic anhydride has a hazard rating of 2 in Sax and Lewis. It is a severe skin and eye irritant.

Sax, N. I., and Lewis, R. J. Dangerous Properties of Industrial Materials 7th Edition, Van Nostrand Reinhold, 1989

Comments:

†Estimated for this report by authors.

Name: bis(perfluoroisopropyl)ketone

Compound group:	Halogenated Ketones, Anhydrides and Esters
Formula:	$(iC_3F_7)_2CO$
Alternate Names:	
CASN:	813-44-5
Normal boiling (nbp °C):	73
Vapor pressure (atm at 298 K):	.15†
Heat capacity at (J/K-mol at 298 K):	280†
Heat of Vaporization (kJ/mol at nbp):	29.7†
Source:	PCR Incorporated, Gainesville, FL 32602 800-331-6313
Price:	$160.00/25g

Toxicity: There are no toxicity data on this compound. Note however the toxic properties of hexafluoroacetone.

Comments: Comparison of the fire suppressant capacity of this compound with hexafluoroacetone will highlight heat capacity effects.

†Estimated for this report by authors.

Name: methyltrifluoroacetate

Compound group:	Halogenated Ketones, Anhydrides and Esters
Formula:	CF_3COOCH_3
Alternate Names:	
CASN:	431-47-0
Normal boiling (nbp °C):	44
Vapor pressure (atm at 298 K):	.4†
Heat capacity at (J/K-mol at 298 K):	113†
Heat of Vaporization (kJ/mol at nbp):	32†
Source:	PCR Incorporated, Gainesville, FL 32602 800-331-6313
Price:	$130.00/100g

Toxicity: There are no toxicity data on this compound. From Sax and Lewis one notes that fluorinated esters have a general lower toxicity rating, 2, than the ketones

Sax, N. I., and Lewis, R. J. Dangerous Properties of Industrial Materials 7th Edition, Van Nostrand Reinhold, 1989.

Comments: This compound is selected with the view that it will be studied in tandem with the brominated compound.

†Estimated for this report by authors.

Name: 3-bromo-1,1,1-trifluoropropanone

Compound group:	Halogenated Ketones, Anhydrides and Esters
Formula:	CF_3COCH_2Br
Alternate Names:	
CASN:	431-35-6
Normal boiling (nbp °C):	86
Vapor pressure (atm at 298 K):	.08†
Heat capacity at (J/K-mol at 298 K):	113†
Heat of Vaporization (kJ/mol at nbp):	32†
Source:	PCR Incorporated, Gainesville, FL 32602 800-331-6313
Price:	$140.00/100g

Toxicity: There are no toxicity data. Toxicity properties should not be any better than the hexafluoroacetone.

Comments: 1,1,1 trifluoroacetone can be purchased and it should be possible to brominate this compound. Comparison with the non-brominated compounds should be extremely interesting.

†Estimated for this report by authors.

Name: bromopentafluoroacetone

Compound group:	Halogenated Ketones, Anhydrides and Esters
Formula:	$BrCF_2COCF_3$
Alternate Names:	

CASN:	815-23-6
Normal boiling (nbp °C):	31
Vapor pressure (atm at 298 K):	.9†
Heat capacity at (J/K-mol at 298 K):	126†
Heat of Vaporization (kJ/mol at nbp):	26.4
Source:	No commercial source was identified
Price:	na

Toxicity: There are no toxicity data on bromopentafluoroacetone. However there is no reason to think that the reactivity of hexafluoroacetone will be decreased by bromination.

Comments: Bromopentafluoroacetone can be prepared from the reaction of bromine with pentafluoropropenol-2 following by beta-dehydrobromination of the pentafluoro-1,2ibromopropanol-2 by heating in N-methylpyrollidone. It is a liquid with an unpleasant odor, soluble in common solvents. In water it forms a hydrate. It is a lachrymator.

This compound is selected for comparison with hexafluoroacetone and will give direct information on the effect of bromine.

Belenki, G. G., Fokin, A. V., Rondarev, D. S., Ryazanovam R. M., Sokolov, S. V., Sterlin, S. R., Voronkov, Zeifman, Y. V. "Fluoroaliphatic Compounds" in Synthesis of Fluoroorganic Compounds, (Knunyants, I. L. and Yakobson, I. L, Editors) Springer-Verlag, New York, pp 3- 108, 1985

†Estimated for this report by authors, na = not available

Name: bromomethyltrifluoroacetate

Compound group:	Halogenated Ketones, Anhydrides and Esters
Formula:	CF_3COOCH_2Br
Alternate Names:	

CASN:	116478-92-4
Normal boiling (nbp °C):	105[†]
Vapor pressure (atm at 298 K):	.03[†]
Heat capacity at (J/K-mol at 298 K):	126[†]
Heat of Vaporization (kJ/mol at nbp):	33.7[†]
Source:	No commercial source was identified
Price:	na

Toxicity: There are no toxicity data. Toxic properties may be similar to other esters.

Comments: It should be possible to brominate the methyltrifluoroacetate. Studying the brominated and non-brominated compounds will lead to important information on the effect of bromine.

[†] Estimated for this report by authors, na = not available

Name: perfluoropropene

Compound group:	Unsaturated Halocarbons
Formula:	C_3F_6
Alternate Names:	Hexafluoropropene

CASN:	116-15-4
Normal boiling (nbp °C):	-29
Vapor pressure (atm at 298 K):	6.42
Heat capacity at (J/K-mol at 298 K):	116
Heat of Vaporization (kJ/mol at nbp):	21
Source:	PCR Incorporated, Gainesville, FL 32602 800-331-6313
Price:	$105.00/1kg

Toxicity: Sax and Lewis assign a hazard rating of 3. It is rated as mildly toxic by inhalation. ihl-rat LC50:11200mg/m^3/4H, ihl-mus LC50: 750 ppm/4H

Larsen has summarized findings on the possible uses of this compound as an anaesthetic. With mixtures in the 50-75% range anaesthetic effects were mild. However convulsions and delayed death also occurred.

Sax, N. I., and Lewis, R. J. Dangerous Properties of Industrial Materials 7th Edition, Van Nostrand Reinhold, 1989

Larsen, E. R. "Fluorine Compounds in Anaesthesiology" in Fluorine Chemistry Reviews, (Tarrant, P., Editor.) Marcel Dekker, New York, 1969

Comments: This compound is selected to determine the effect of double bonds on fire suppressant activity. It is a base for comparisons with various brominated compounds.

Name: perfluorobutene-2

Compound group: Unsaturated Halocarbons
Formula: C_4F_8-2
Alternate Names: 1,1,1,2,3,4,4,4,octafluorobutene

CASN: 360-89-4
Normal boiling (nbp °C): 0
Vapor pressure (atm at 298 K): 2.62
Heat capacity at (J/K-mol at 298 K): 138[†]
Heat of Vaporization (kJ/mol at nbp): 21[†]
Source: PCR Incorporated, Gainesville, FL 32602 800-331-6313
Price: $200.00/100g

Toxicity: Sax and Lewis assign a hazard rating of 1. It is mildly toxic by inhalation; ihl-rat LCLo:6100 ppm/4H

Sax, N. I., and Lewis, R. J. Dangerous Properties of Industrial Materials 7th Edition, Van Nostrand Reinhold, 1989

Comments: The isomer perfluoroisobutene is a deadly poison by inhalation. In studies with this compound some thought should be given to the possibility of conversion to this toxic isomer.

[†] Estimated for this report by authors.

Name: perfluorotoluene

Compound group:	Unsaturated Halocarbons
Formula:	$CF_3C_6F_5$
Alternate Names:	
CASN:	434-64-0
Normal boiling (nbp °C):	104
Vapor pressure (atm at 298 K):	.03†
Heat capacity at (J/K-mol at 298 K):	207†
Heat of Vaporization (kJ/mol at nbp):	34†
Source:	PCR Incorporated, Gainesville, FL 32602 800-331-6313
Price:	$156.00/50g

Toxicity: Perfluorotoluene is given a hazard rating of 1 by Sax and Lewis and is stated to be mildly toxic by inhalation. Larsen has summarized studies on the possible use of this compound as an anaesthetic and reported delayed death at levels as low as 0.5-0.9%

Sax, N. I., and Lewis, R. J. Dangerous Properties of Industrial Materials 7th Edition, Van Nostrand Reinhold, 1989

Larsen, E. R. "Fluorine Compounds in Anaesthesiology" in Fluorine Chemistry Reviews, (Tarrant, P., Editor.) Marcel Dekker, New York, 1969

Comments: This compound has been selected in order to test the effects arising from a fully fluorinated aromatic structure.

†Estimated for this report by authors.

Name: 1,1,3,3,3-pentafluoropropene-1

Compound group:	Unsaturated Halocarbons
Formula:	$CF_3CH{=}CF_2$
Alternate Names:	
CASN:	690-27-7
Normal boiling (nbp °C):	-21
Vapor pressure (atm at 298 K):	5[†]
Heat capacity at (J/K-mol at 298 K):	109[†]
Heat of Vaporization at nbp (kJ/mol):	23[†]
Source:	PCR Incorporated, Gainesville, FL 32602 800-331-6313
Price:	$500.00/100g

Toxicity: There are no toxicity data.

Comments: This compound has been selected for comparison with the fully fluorinated propene. Important information will also be obtained through comparison with the compound where the hydrogen is replaced by bromine.

[†] Estimated for this report by authors.

Name: 3,3,3-trifluoropropene

Compound group:	Unsaturated Halocarbons
Formula:	$CF_3CH=CH_2$
Alternate Names:	

CASN:	677-21-4
Normal boiling (nbp °C):	-17
Vapor pressure (atm at 298 K):	4[†]
Heat capacity at (J/K-mol at 298 K):	92[†]
Heat of Vaporization (kJ/mol at nbp):	24[†]
Source:	PCR Incorporated, Gainesville, FL 32602 800-331-6313
Price:	$220.00/500g

Toxicity: There is no toxicity data.

Comments: This compound has been selected for comparison with the fully fluorinated propene. Important information will also be obtained through comparison with the compound where the hydrogen is replaced by bromine.

[†] Estimated for this report by authors.

Name: 1,2-bis(perfluoro-n-butyl)ethylene

Compound group:	Unsaturated Halocarbons
Formula:	$(nC_4F_9)CH{=}CH(nC_4F_9)$
Alternate Names:	

CASN:	84551-43-9
Normal boiling (nbp °C):	132
Vapor pressure (atm at 298 K):	.006†
Heat capacity at (J/K-mol at 298 K):	377†
Heat of Vaporization (kJ/mol at nbp):	36†
Source:	Produits Chimiques Ugine Kuhlmann, France
Price:	na

Toxicity: This compound has been used as a blood substitute. Short-term toxic properties should therefore be satisfactory

Comments: The boiling point is probably too high for use as a fire suppressant. However the ready availability means that tests can be made immediately. The data summarized by Larsen indicate that flammability limits are lowered by the presence of the double bond. It will be very interesting to see how this is carried over to this compound which is extremely inert. A particularly interesting property is that it is readily emulsified. This may prove to be an interesting way of delivering the suppressant.

Riess, J. G. and LeBlanc, M. "Perfluoro Compounds as Blood Substitutes" Angewandte Chemie, International Edition, 9, 621-634, 1978

Larsen, E. R. "Fluorine Compounds in Anaesthesiology" in Fluorine Chemistry Reviews, (Tarrant, P., Editor.) Marcel Dekker, New York, 1969

†Estimated for this report by authors, na = not available

Name: 3-bromoperfluoropropene

Compound group:	Unsaturated Halocarbons
Formula:	$BrCF_2CF=CF_2$
Alternate Names:	

CASN:	431-56-1
Normal boiling (nbp °C):	28
Vapor pressure (atm at 298 K):	1[†]
Heat capacity at (J/K-mol at 298 K):	121[†]
Heat of Vaporization (kJ/mol at nbp):	27[†]
Source:	No commercial source was identified
Price:	na

Toxicity:

Comments: This compound is selected for comparison with the fully and partially fluorinated propenes. 3-Bromoperfluoropropene can be synthesized through the reaction of dibromodifluoromethane in the presence of benzoyl peroxide at 100° C. The major product, 3-dibromo-1,1,2,3,3-pentafluoropropane can be dehydro-brominated in the presence of KOH to form the desired compound.

Tarrant, P. Lovelace, A. M. and Lilyquist, M. R. "Free Radical Additions Involving Fluorine Compounds," Journal of the American Chemical Society, 77, 2783-2787

Cocia, A. T., "Free Radical Addition to Trifluoroethylene," Journal of Organic Chemistry, 2995-2996, 26, 1961

[†] Estimated for this report by authors, na = not available

Name: 1-bromoperfluoropropene

Compound group:	Unsaturated Halocarbons
Formula:	$CF_3CF{=}CFBr$
Alternate Names:	
CASN:	14003-53-3 14003-61-3
Normal boiling (nbp °C):	$30^{\dagger}$
Vapor pressure (atm at 298 K):	$1^{\dagger}$
Heat capacity at (J/K-mol at 298 K):	$121^{\dagger}$
Heat of Vaporization (kJ/mol at nbp):	$27^{\dagger}$
Source:	No commercial source was identified
Price:	na

Toxicity: There are no toxicity data.

Comments: This compound has been selected for comparison with the fully and partially fluorinated substances that are also recommended for study.

†Estimated for this report by authors, na = not available

Name: 1,2-bis(perfluoromethyl)ethylene

Compound group:	Unsaturated Halocarbons
Formula:	$CF_3CH{=}CHCF_3$
Alternate Names:	

CASN:	66711-86-2
Normal boiling (nbp °C):	6
Vapor pressure (atm at 298 K):	1.6[†]
Heat capacity at (J/K-mol at 298 K):	130[†]
Heat of Vaporization (kJ/mol at nbp):	26[†]
Source:	No commercial source was identified
Price:	na

Toxicity:

There are no toxicity data for this compound. The perfluorobutyl analogy is a blood substitute and it may well be that the properties of this compound will also be favorable. However, it is known that the reactivity of these compound decreases as the size of the perfluorinated alkyls are increased. It may well be that there is an optimum size for fire suppression purposes.

Riess, J. G. and LeBlanc, M. "Perfluoro Compounds as Blood Substitutes" Angewandte Chemie, International Edition, 9, 621-634, 1978

Comments:

This compound is proposed in the expectation that the brominated analog will also be studied. Larsen has shown that the presence of a double bond generally lowers the flammability limit. It is expected that bromination will raise this value. Comparisons with perfluorinated butene-2, as well as, 1,1,1,2,3,4,4,4-octafluorobutane will provide an extremely important set of results regarding the role of double bond in flame suppression.

This compound has been synthesized via the fluorination of fumaric acid by SF_4 at 130°C. An alternate synthetic path is telomerization of perfluoroethylene with methyl iodide.

Larsen, E. R. "Fluorine Compounds in Anaesthesiology" in Fluorine Chemistry Reviews, (Tarrant, P., Editor.) Marcel Dekker, New York, 1969

Hasek, W. R., Smith, W. C. and Engelhardt, V. A., "The Chemistry of Sulfur Tetrafluoride. II. The Fluorination of Organic Carbonyl Compounds" Journal of the American Chemical Society, 82, 543-551, 1960

[†] Estimated for this report by authors, na = not available

Name: 1-bromoperfluoromethyl-2-perfluoromethylethylene

Compound group:	Unsaturated Halocarbons
Formula:	$CF_2BrHC=CHCF_3$
Alternate Names:	

CASN:	na
Normal boiling (nbp °C):	57[†]
Vapor pressure (atm at 298 K):	.1[†]
Heat capacity at (J/K-mol at 298 K):	138[†]
Heat of Vaporization (kJ/mol at nbp):	30[†]
Source:	No commercial source was identified
Price:	na

Toxicity: There are no toxicity data.

Comments: This compound has been selected for comparison with 1,2 bis(perfluoromethyl)ethylene.

[†] Estimated for this report by authors, na = not available

Name: 1-bromo-bis(perfluoromethyl)ethylene

Compound group:	Unsaturated Halocarbons
Formula:	$CF_3BrC{=}CHCF_3$
Alternate Names:	

CASN:	400-41-9
Normal boiling (nbp °C):	65[†]
Vapor pressure (atm at 298 K):	.06[†]
Heat capacity at (J/K-mol at 298 K):	143[†]
Heat of Vaporization (kJ/mol at nbp):	33[†]
Source:	No commercial source was available
Price:	na

Toxicity: There are no toxicity data.

Comments: This compound is selected with the expectation that it will be studied with the non-brominated analog. The comparison of the results from the two studies will yield information on the effect of bromine on fire suppression properties.

It should be possible to synthesize this compound through the hydrobromination of perfluorobutyne-2.

[†] Estimated for this report by authors, na = not available

Name: tetris(perfluoromethyl)ethylene

Compound group:	Unsaturated Halocarbons
Formula:	$(CF_3)_2C=C(CF_3)_2$
Alternate Names:	

CASN:	360-57-6
Normal boiling (nbp °C):	55
Vapor pressure (atm at 298 K):	$.28^{\dagger}$
Heat capacity at (J/K-mol at 298 K):	180
Heat of Vaporization (kJ/mol at nbp):	29
Source:	No commercial source was available
Price:	na

Toxicity: The tetris(perfluoro-n-butyl)ethylene version of this molecule is a blood substitute. This molecule is proposed for study in the expectation that it will have similar favorable properties.

Geyer, R. P., "Perfluorochemicals as Oxygen Transport Vehicles" in Blood Substitutes (Chang, T. M. S. and Geyer, R. P., Editors) Marcel Dekker, New York, pp31-49, 1989

Comments: Possible synthesis routes are outlined in the paper by Bell et al.

Bell, A. N., Fields, R. and Haszeldine, R. N., "Fluoro-olefin Chemistry. Part 13. A Further Route to Perfluoro-2,3-dimethylbut-2-ene and the Photochemical Rearrangement of Some Perfluoro-Alkyl Olefins," J. Chem. Soc, 487, 1980

†Estimated for this report by authors, na = not available

Name: tetrafluorodimethyl ether

Compound group:	Halogenated Ethers
Formula:	CF_2HOHCF_2
Alternate Names:	

CASN:	1691-17-4
Normal boiling (nbp °C):	2
Vapor pressure (atm at 298 K):	2[†]
Heat capacity at (J/K-mol at 298 K):	92[†]
Heat of Vaporization (kJ/mol at nbp):	24.5[†]
Source:	PCR Incorporated, Gainesville, FL 32602 800-331-6313
Price:	$150.00/100g

Toxicity: There are no toxicity data.

Comments: This is the starting material for bromination. Comparison with the brominated compound can lead to important mechanistic information on chemical fire suppressant mechanisms.

[†] Estimated for this report by authors.

Name: pentafluordimethyl ether

Compound group:	Halogenated Ethers
Formula:	CF_2HOCF_3
Alternate Names:	

CASN:	3822-68-2
Normal boiling (nbp °C):	-35
Vapor pressure (atm at 298 K):	7[†]
Heat capacity at (J/K-mol at 298 K):	109[†]
Heat of Vaporization (kJ/mol at nbp):	21.2[†]
Source:	PCR Incorporated, Gainesville, FL 32602 800-331-6313
Price:	$150.00/100g

Toxicity: There are no toxicity data.

Comments: This is the starting material for bromination. Comparison with the brominated compound can lead to important mechanistic information on chemical fire suppressant mechanisms.

[†] Estimated for this report by authors, na = not available

Name: 2-chloro-1-(difluoromethoxy)-1,1,2-trifluoroethane

Compound group:	Halogenated Ethers
Formula:	CHF_2OCF_2CHFCl
Alternate Names:	enflurane, enthrane, methylfluorether
CASN:	13838-16-9
Normal boiling (nbp °C):	56.5
Vapor pressure (atm at 298 K):	.29
Heat capacity at (J/K-mol at 298 K):	162[†]
Heat of Vaporization (kJ/mol at nbp):	29.4[†]
Source:	Anaquest, 2005 West Beltline Highway, Madison Wisconsin 53713-2318
Price:	$400.00/750 cm^3

Toxicity: This compound is a widely used anaesthetic. Health effects are well documented. It is considered to be mildly toxic by inhalation, ingestion and subcutaneous routes and is given a hazard rating of 2 by Sax and Lewis

Comments: As a successful anaesthetic it is disqualified as a fire suppressant. We have selected this compound in order to study it in tandem with the brominated version.

[†] Estimated for this report by authors.

Name: isoflurane

Compound group:	Halogenated Ethers
Formula:	$CF_3CHClOCHF_2$
Alternate Names:	
CASN:	26775-46-7
Normal boiling (nbp °C):	48.5
Vapor pressure (atm at 298 K):	.32
Heat capacity at (J/K-mol at 298 K):	167[†]
Heat of Vaporization (kJ/mol at nbp):	28.7[†]
Source:	Anaquest, 2005 West Beltline Highway, Madison Wisconsin 53713-2318
Price:	\$400.00/750 cm^3

Toxicity: This is a well known anaesthetic. A great deal of toxicity data exists.

Comments: As an anaesthetic this is not an acceptable fire suppressant. However, it is known to be non-flammable in anaesthetic contexts and since it is readily available it will be interesting to compare this compound with its structural isomer, 2-chloro-1-(difluoromethoxy)-1,1,2-trifluoroethane or enflurane (see other data sheet).

[†] Estimated for this report by authors.

Name: perfluoro-2-butyltetrahydrofuran

Compound group:	Halogenated Ethers
Formula:	$C_4F_9C_4F_7O$
Alternate Names:	
CASN:	335-36-4
Normal boiling (nbp °C):	103
Vapor pressure (atm at 298 K):	.033†
Heat capacity at (J/K-mol at 298 K):	na
Heat of Vaporization (kJ/mol at nbp):	33.5†
Source:	PCR Incorporated, Gainesville, FL 32602 800-331-6313
Price:	$85.00/500g

Toxicity: This compound has been used as a blood substitute. It should not have any short term health effects.

Comments: The vapor pressure of this compound is probably too low for fire suppressant use. However, its availability and favorable toxic properties suggest that studies be carried out as a preliminary to further test with the side chain removed and with bromine substitution.

†Estimated for this report by authors, na = not available

Name: bis(bromodifluoroethyl) ether

Compound group:	Halogenated Ethers
Formula:	$BrCF_2OCF_2Br$
Alternate Names:	
CASN:	na
Normal boiling (nbp °C):	25†
Vapor pressure (atm at 298 K):	1†
Heat capacity at (J/K-mol at 298 K):	117†
Heat of Vaporization (kJ/mol at nbp):	26.7†
Source:	No commercial source was identified
Price:	na

Toxicity:

Comments: This is one of the compounds that is being synthesized for EPA. First priority should be assigned to determining whether this compound can be photolyzed in the troposphere.

†Estimated for this report by authors, na = not available

Name: 1-bromo,1,1,3,3,3-pentafluorodimethyl ether

Compound group:	Halogenated Ethers
Formula:	CF_2BrOCF_3
Alternate Names:	
CASN:	na
Normal boiling (nbp °C):	-30[†]
Vapor pressure (atm at 298 K):	6[†]
Heat capacity at (J/K-mol at 298 K):	104[†]
Heat of Vaporization (kJ/mol at nbp):	24.7[†]
Source:	No commercial source was identified
Price:	na

Toxicity: There are no toxicity data.

Comments: The compound is being synthesized through an EPA-supported program. An important issue is whether the addition of the bromine will change the photolytic property sufficiently.

[†] Estimated for this report by authors, na = not available

Name: bromoenflurane

Compound group:	Halogenated Ethers
Formula:	$CBrF_2OCF_2CHFCl$
Alternate Names:	

CASN:	na
Normal boiling (nbp °C):	67[†]
Vapor pressure (atm at 298 K):	.2[†]
Heat capacity at (J/K-mol at 298 K):	175[†]
Heat of Vaporization (kJ/mol at nbp):	30.3[†]
Source:	No commercial source was identified
Price:	na

Toxicity:	There are no toxicity data. The nonbrominated version of the compound is the well known anaesthetic enflurane. One does not expect that toxicity will decrease with behavior.
Comments:	The nonbrominated compound is easily obtainable. Bromination should be straightforward. Studies on the fire suppressant capabilities of the pair of compounds should be extremely informative.

[†] Estimated for this report by authors, na = not available

Name: octafluorofuran

Compound group:	Halogenated Ethers
Formula:	C_4F_8O
Alternate Names:	
CASN:	773-14-8
Normal boiling (nbp °C):	$50^{\dagger}$
Vapor pressure (atm at 298 K):	$.33^{\dagger}$
Heat capacity at (J/K-mol at 298 K):	$151^{\dagger}$
Heat of Vaporization (kJ/mol at nbp):	$28.8^{\dagger}$
Source:	No commercial source was identified
Price:	na

Toxicity: There are no toxicity data. The perfluorobutyl substituted compound is a blood substitute. This may mean that the toxic properties of this compound will be within acceptable limits.

Comments: It may be possible synthesize this compound through the electrofluorination of tetrahydrofuran.

†Estimated for this report by authors, na = not available

Name: 3-bromoperfluorofuran

Compound group:	Halogenated Ethers
Formula:	BrC_4F_7O
Alternate Names:	
CASN:	na
Normal boiling (nbp °C):	105†
Vapor pressure (atm at 298 K):	.03†
Heat capacity at (J/K-mol at 298 K):	159†
Heat of Vaporization (kJ/mol at nbp):	33.7†
Source:	No commercial source was identified
Price:	na

Toxicity: There are no toxicity on this compound.

Comments: It may be possible to synthesize this compound through the electrofluorination of tetrahydrofuran and then brominating the incompletely fluorinated compounds.

†Estimated for this report by authors, na = not available

Name: bis(perfluoromethyl) thioether

Compound group:	Miscellaneous
Formula:	CF_3SCF_3
Alternate Names:	
CASN:	371-78-87
Normal boiling (nbp °C):	-22.2
Vapor pressure (atm at 298 K):	6.1
Heat capacity at (J/K-mol at 298 K):	126†
Heat of Vaporization (kJ/mol at nbp):	25.1†
Source:	No commercial source was identified
Price:	na

Toxicity: No toxicity data are available. However, note that the thio-analog of the well known anaesthetic methoxyflurane has been synthesized and tested and showed enhanced properties. This general trend may hold for all such substitutions.

Le Blanc, M. and Riess, J. G., "Artificial Blood Substitutes Based on Perfluorochemicals" in Preparation, Properties and Industrial Applications of Organofluorine Compounds, (Banks, R. E., Editor.) Halsted Press, New York, pp 83-138 ,1982

Comments: Bis(perfluoromethyl)thioether is not available from any commercial source. It should be possible to synthesize the compound via electrochemical fluorination (Simons Process) starting with dimethyl ether. The process is not complete. Thus it should also be possible to recover thioethers with one or more hydrogens. These should be convenient starting products for bromination, if these compounds are necessary for subsequent study.

This compound has also been prepared via the photolysis of the disulfide.

Brandt, G. A. R., Emeleus, H. J., and Haszeldine, R. N., "Organometallic and Organometalloidal Fluorine Compounds," Journal of the Chemical Society, 2198-2205, 1952

†Estimated for this report by authors, na = not available

Name: tris(perfluoromethyl) amine

Compound group:	Miscellaneous
Formula:	$(CF_3)_3N$
Alternate Names:	
CASN:	432-03-1
Normal boiling (nbp °C):	-10.1
Vapor pressure (atm at 298 K):	3.9
Heat capacity at (J/K-mol at 298 K):	167[†]
Heat of Vaporization (kJ/mol at nbp):	25.1
Source:	No commercial source was available
Price:	na

Toxicity: No toxicity data are available. Higher members of this series are used as blood substitutes. This may be an indication that there will be no serious health effects at least in the short term.

Comments: Tris(perfluoromethyl) amine is not available from any commercial source. It is readily prepared from trimethyl amine via electrochemical fluorination (Simons Process). Should initial tests on these compounds prove to be satisfactory the next step will be to replace one or two of the fluorine by bromine. This can be accomplished by brominating the hydrogens from the incomplete fluorination of the trimethyl amine.

Pawelke, G., Heyder, F. and Burger, H., "Halogen Exchange of Fluoroalkyl Amines , Synthesis of Polychloro- and Bromo-Trialkylamines Journal of Fluorine Chemistry, 20, 53-63, 1982.

[†] Estimated for this report by authors, na = not available

Name: iodotrifluoromethane

Compound group:	Halons Containing Iodine
Formula:	CF_3I
Alternate Names:	perfluoromethyl iodide, trifluoromethyl iodide, halon 13001
CASN:	2314-97-8
Normal boiling point (nbp °C):	-22.5
Vapor pressure (atm at 298 K):	na
Heat capacity (J/K-mol at 298 K):	70.9
Heat of Vaporization (kJ/mol at nbp):	22[†]
Source:	Aldrich Chemical Company, Milwaukee, WI, 53233, 800-558-9160
Price:	$255.90/100 g

Toxicity: No published data were identified for this compound. Researchers should use caution.

Comments: Fire suppression references:

Lask, G. and Wagner, H.Gg., "Influence of Additives on the Velocity of Laminar Flames," Eight Symposium (International) on Combustion, pp. 432-438, Williams and Wilkins, Baltimore, 1962.

Sheinson, R.S., Gellene, G.I., Williams, F.W., and Hahn, J.E., "Quantification of Fire Suppression Action on Liquid Pool Fires," Abstract for paper presented at the 1978 Fall Technical Meeting of the Eastern Section of the Combustion Institute, Miami, FL, 29 November-1 December 1978.

Sheinson, R.S., Penner-Hahn, J.E., and Indritz, D., "The Physical and Chemical Action of Fire Suppressants, Fire Safety Journal, accepted for publication.

[†] Estimated for this report by authors, na = not available

Name: chlorodifluoroiodomethane

Compound group:	Halons Containing Iodine
Formula:	CF_2ClI
Alternate Names:	halon 12101

CASN:	420-49-5
Normal boiling point (nbp °C):	33
Vapor pressure (atm at 298 K):	na
Heat capacity (J/K-mol at 298 K):	76†
Heat of Vaporization (kJ/mol at nbp):	27†
Source:	No commercial source was identified.
Price:	na

Toxicity: No published data were identified for this compound. Researchers should use caution.

Comments: A preparative procedure is available in the literature.

Burton, D.J., Shin-Ya, S., and Kesling, H.S., "Preparation of Halo-F-Methanes via Potassium Fluoride-Halogen Cleavage of Halo-F-Methylphosphonium Salts," Journal of Fluorine Chemistry, vol. 20, pp. 89-97, 1982.

No fire suppression measurements were identified for this compound.

†Estimated for this report by authors, na = not available

Name: 1-bromo-1,1,2,2-tetrafluoro-2-iodoethane

Compound group:	Halons Containing Iodine
Formula:	CF_2BrCF_2I
Alternate Names:	1-bromo-2-iodotetrafluoromethane, halon 24011

CASN:	471-70-5
Normal boiling point (nbp °C):	78
Vapor pressure (atm at 298 K):	na
Heat capacity (J/K-mol at 298 K):	124†
Heat of Vaporization (kJ/mol at nbp):	31†
Source:	PCR Incorporated, Gainesville, FL 32602, 800-331-6313
Price:	$195/100 g

Toxicity: No published data were identified for this compound. Researchers should use caution.

Comments: No fire suppression measurements were identified for this compound.

†Estimated for this report by authors, na = not available

Name: 1,1,2,2-tetrafluoro-1,2-diiodoethane

Compound group: Halons Containing Iodine
Formula: CF_2ICF_2I
Alternate Names: halon 24002

CASN: 354-65-4
Normal boiling point (nbp °C): 112
Vapor pressure (atm at 298 K): na
Heat capacity (J/K-mol at 298 K): 126†
Heat of Vaporization (kJ/mol at nbp): 34†
Source: PCR Incorporated, Gainesville, FL 32602, 800-331-6313
Price: $165/100 g

Toxicity: No published data were identified for this compound. Researchers should use caution.

Comments: No fire suppression measurements were identified for this compound.

†Estimated for this report by authors, na = not available

Name: iodomethane

Compound group:	Halons Containing Iodine
Formula:	CH_3I
Alternate Names:	methyl iodide, halon 10001
CASN:	74-88-4
Normal boiling point (nbp °C):	42.4
Vapor pressure (atm at 298 K):	0.53
Heat capacity (J/K-mol at 298 K):	44.1
Heat of Vaporization (kJ/mol at nbp):	27.4
Source:	Aldrich Chemical Company, Milwaukee, WI, 53233, 800-0558-9160
Price:	$74.70/500 g

Toxicity: Sax and Lewis: HR:3, High toxic, fire, or reactivity hazard Poison, suspected carcinogen, a human skin irritant, human mutagenic data.

Sigma Aldrich: Carcinogen, highly toxic, vesicant, mutagen

Sax, N.I. and Lewis, Sr., R.J., Dangerous Properties of Industrial Materials, 7th Ed., Van Nostrand Reinhold, New York, 1989.

Lenga, R.E., The Sigma-Aldrich Library of Chemical Safety Data, Sigma-Aldrich Corporation, 1985.

Comments: Fire suppression references:

de C. Ellis, O.C., "Extinction of Petrol Fires by Methyl Iodide," Nature, vol. 161, pp. 402-403, 13 March 1948.

"Final Report on Fire Extinguishing Agents for the Period September 1, 1947 to June 30, 1950," Purdue Research Foundation and Department of Chemistry, Purdue University, West Lafayette, IN, July 1950.

Rosser, W.A., Wise, H., and Miller, J., "Mechanism of Combustion Inhibition by Compounds Containing Halogen," Seventh Symposium (International) on Combustion, pp. 175-182, Butterworths, London, 1958.

Homann, K.H. and Poss, R., "The Effect of Pressure on the Inhibition of Ethylene Flames," Combustion and Flame, vol. 18, pp. 300-302, April 1972.

Westbrook, C.K., "Inhibition of Hydrocarbon Oxidation in Laminar Flames and Detonations by Halogenated Compounds," Nineteenth Symposium (International) on Combustion, pp. 127-141, The Combustion Institute, Pittsburgh, 1982.

Name: iodoethane

Compound group:	Halons Containing Iodine
Formula:	CH_3CH_2I
Alternate Names:	ethyl iodide, halon 20001

CASN:	75-03-6
Normal boiling point (nbp °C):	72.3
Vapor pressure (atm at 298 K):	0.18
Heat capacity (J/K-mol at 298 K):	67.8
Heat of Vaporization (kJ/mol at nbp):	29.4
Source:	Aldrich Chemical Company, Milwaukee, WI, 53233, 800-558-9160
Price:	$107.50/5 g

Toxicity: Sax and Lewis: HR:3, High toxic, fire, or reactivity hazard

Sigma Aldrich: Toxic, severe irritant, vesicant

Sax, N.I. and Lewis, Sr., R.J., Dangerous Properties of Industrial Materials, 7th Ed., Van Nostrand Reinhold, New York, 1989.

Lenga, R.E., The Sigma-Aldrich Library of Chemical Safety Data, Sigma-Aldrich Corporation, 1985.

Comments: Fire suppression references:

Jorissen, W.P., Booy, J., and van Heiningen, J., "Reaction-Regions XXII. On the Prevention of Explosive Reactions in Gas and Vapour Mixtures by Small Amounts of Various Substances," Recueil des Travaux Chimiques des Pay-Bas, vol. 51, pp. 868-877, 15 July 1932.

"Final Report on Fire Extinguishing Agents for the Period September 1, 1947 to June 30, 1950," Purdue Research Foundation and Department of Chemistry, Purdue University, West Lafayette, IN, July 1950.

Westbrook, C.K., "Inhibition of Hydrocarbon Oxidation in Laminar Flames and Detonations by Halogenated Compounds," Nineteenth Symposium (International) on Combustion, pp. 127-141, The Combustion Institute, Pittsburgh, 1982.

Name: 1-iodopropane

Compound group:	Halons Containing Iodine
Formula:	$CH_3CH_2CH_2I$
Alternate Names:	propyl iodide, halon 30001

CASN:	107-08-4
Normal boiling point (nbp °C):	102.4
Vapor pressure (atm at 298 K):	0.6
Heat capacity (J/K-mol at 298 K):	88.3
Heat of Vaporization (kJ/mol at nbp):	32.1
Source:	Aldrich Chemical Company, Milwaukee, WI, 53233, 800-558-9160
Price:	$47.30/500 g

Toxicity:

Sax and Lewis: HR:3, High toxic, fire, or reactivity hazard
Poison by intraperitoneal route, experimental neoplastigen, very mildly toxic by inhalation

Sigma Aldrich: Harmful if swallowed, inhaled, or absorbed through skin; may cause irritation; chronic effects: carcinogen.

Sax, N.I. and Lewis, Sr., R.J., Dangerous Properties of Industrial Materials, 7th Ed., Van Nostrand Reinhold, New York, 1989.

Lenga, R.E., The Sigma-Aldrich Library of Chemical Safety Data, Sigma-Aldrich Corporation, 1985.

Comments:

Fire suppression references:

Rosser, W.A., Wise, H., and Miller, J., "Mechanism of Combustion Inhibition by Compounds Containing Halogen," Seventh Symposium (International) on Combustion, pp. 175-182, Butterworths, London, 1958.

Name: 1,1,1,2,2,3,3-heptafluoro-3-iodopropane

Compound group:	Halons Containing Iodine
Formula:	$CF_3CF_2CF_2I$
Alternate Names:	perfluoropropyl iodide, halon 37001

CASN:	754-34-7
Normal boiling point (nbp °C):	40
Vapor pressure (atm at 298 K):	na
Heat capacity (J/K-mol at 298 K):	197†
Heat of Vaporization (kJ/mol at nbp):	28†
Source:	Aldrich Chemical Company, Milwaukee, WI, 53233, 800-558-9160
Price:	$76.70/25 g

Toxicity: No published data were identified for this compound. Researchers should use caution.

Comments: No fire suppression measurements were identified for this compound.

†Estimated for this report by authors, na = not available

Name: sulfur fluoride

Compound group:	Sulfur halides
Formula:	SF_6
Alternate Names:	sulfur hexafluoride

CASN:	2551-62-4
Normal boiling point (nbp °C):	-63.8 (sublimes)
Vapor pressure (atm at 298 K):	21.8
Heat capacity (J/K-mol at 298 K):	97.0
Heat of Vaporization (kJ/mol at nbp):	23.6
Source:	Aldrich Chemical Company, Milwaukee, WI, 53233, 800-558-9160
Price:.	$96.40/227 g

Toxicity: Sax and Lewis: HR:1, Low toxic, fire, or reactivity hazard
Chemically inert and considered to be physiologically inert as well.

Sax, N.I. and Lewis, Sr., R.J., Dangerous Properties of Industrial Materials, 7th Ed., Van Nostrand Reinhold, New York, 1989.

Comments: Fire suppression references:

"Final Report on Fire Extinguishing Agents for the Period September 1, 1947 to June 30, 1950," Purdue Research Foundation and Department of Chemistry, Purdue University, West Lafayette, IN, July 1950.

Moran, Jr., H.E. and Bertschy, A.W., Flammability Limits for Mixtures of Hydrocarbon Fuels, Air, and Halogen Compounds, NRL Report 4121, Engineering Research Branch, Chemistry Division, Naval Research Laboratory, Washington, DC, 25 February 1953.

Miller, W.J., "Inhibition of Low Pressure Flames," Combustion and Flame, vol. 13, pp. 210-212, April 1969.

Sheinson, R.S., Penner-Hahn, J.E., and Indritz, D., "The Physical and Chemical Action of Fire Suppressants, Fire Safety Journal, accepted for publication.

Name: sulfur chloride fluoride

Compound group:	Sulfur halides
Formula:	SF_5Cl
Alternate Names:	sulfur chloropentafluoride

CASN:	13780-57-9
Normal boiling point (nbp °C):	-21
Vapor pressure (atm at 298 K):	na
Heat capacity (J/K-mol at 298 K):	104
Heat of Vaporization (kJ/mol at nbp):	21.7
Source:	PCR Incorporated, Gainesville, FL 32602, 800-331-6313
Price:	$175/25 g ($110 cylinder charge)

Toxicity: Sulfur chloride fluoride has been cited as being as toxic as phosgene by Gage. Phosgene is given a HR rating of 3 (high toxic, fire, or reactivity hazard) by Sax and Lewis and is described as a human poison.

Gage, J.C., "Subacute inhalation toxicity of 109 Industrial Chemicals," British Journal of Industrial Medicine, vol. 27, pp. 1-18, 1970.

Sax, N.I. and Lewis, Sr., R.J., Dangerous Properties of Industrial Materials, 7th Ed., Van Nostrand Reinhold, New York, 1989.

Comments: Fire suppression references:

Sheinson, R.S., Penner-Hahn, J.E., and Indritz, D., "The Physical and Chemical Action of Fire Suppressants, Fire Safety Journal, accepted for publication.

na = not available

Name: sulfur bromide fluoride

Compound group:	Sulfur halides
Formula:	SF_5Br
Alternate Names:	sulfur bromopentafluoride, pentafluorosulfur bromide

CASN:	15607-89-3
Normal boiling point (nbp °C):	3.1
Vapor pressure (atm at 298 K):	na
Heat capacity (J/K-mol at 298 K):	107
Heat of Vaporization (kJ/mol at nbp):	24†
Source:	No commercial source was identified.
Price:	na

Toxicity: No toxicity data were identified in the literature. By analogy with sulfur chloride fluoride, this compound is likely to be at least as toxic as phosgene.

Comments: A preparative procedure is available in the literature.

Kovacina, T.A., Berry, A.D., and Fox, W.B., "Improved Preparation and Purification of Pentafluorosulfur Bromide," Journal of Fluorine Chemistry, vol. 7, pp. 430-432, 1976.

Fire suppression references:

Sheinson, R.S., Penner-Hahn, J.E., and Indritz, D., "The Physical and Chemical Action of Fire Suppressants, Fire Safety Journal, accepted for publication.

†Estimated for this report by authors, na = not available

Name: phosphorus trifluoride

Compound group:	phosphorus-containing compounds
Formula:	PF_3
Alternate Names:	phosphorous fluoride

CASN:	7783-55-3
Normal boiling point (nbp °C):	-101
Vapor pressure (atm at 298 K):	66
Heat capacity (J/K-mol at 298 K):	58.7
Heat of Vaporization (kJ/mol at nbp):	14.6
Source:	Pfaltz and Bauer, Inc., Waterbury, CT, 203-574-0075
Price:	$539.50/100 g plus refundable $95 cylinder charge

Toxicity: Sax and Lewis: HR:3, High toxic, fire, or reactivity hazard
Moderately toxic by inhalation; a severe eye, skin, and mucous membrane irritant.

Sax, N.I. and Lewis, Sr., R.J., Dangerous Properties of Industrial Materials, 7th Ed., Van Nostrand Reinhold, New York, 1989.

Comments: No fire suppression measurements were identified for this compound.

The commercial material is nominally 98% pure. A procedure for its purification has been published.

Liang, S. and Trenary, M., "An Infrared Study of the Symmetric P-F Stretch of PF_3 Chemisorbed on the Pt(111) Surface," Journal of Chemical Physics, vol. 89, pp. 3323-3230, September 1988.

Name: phosphorus trichloride

Compound group:	phosphorus-containing compounds
Formula:	PCl_3
Alternate Names:	phosphorous chloride, chloride of phosphorous

CASN:	7719-12-2
Normal boiling point (nbp °C):	76
Vapor pressure (atm at 298 K):	0.16
Heat capacity (J/K-mol at 298 K):	71.6
Heat of Vaporization (kJ/mol at nbp):	30.5
Source:	Aldrich Chemical Company, Milwaukee, WI, 53233, 800-558-9160
Price:	$75.70/100 g

Toxicity: Sax and Lewis: HR:3, High toxic, fire, or reactivity hazard Poison by inhalation; moderately toxic by ingestion; a corrosive irritant to skin, eyes, and mucous membranes.

Sax, N.I. and Lewis, Sr., R.J., Dangerous Properties of Industrial Materials, 7th Ed., Van Nostrand Reinhold, New York, 1989.

Comments: Fire suppression references:

"Final Report on Fire Extinguishing Agents for the Period September 1, 1947 to June 30, 1950," Purdue Research Foundation and Department of Chemistry, Purdue University, West Lafayette, IN, July 1950.

Lask, G. and Wagner, H.Gg., "Influence of Additives on the Velocity of Laminar Flames," Eight Symposium (International) on Combustion, pp. 432-438, Williams and Wilkins, Baltimore, 1962.

Name: phosphorus bromide difluoride

Compound group:	phosphorus-containing compounds
Formula:	PF_2Br
Alternate Names:	bromodifluorophosphine
CASN:	15597-40-7
Normal boiling point (nbp °C):	-16
Vapor pressure (atm at 298 K):	4.5
Heat capacity (J/K-mol at 298 K):	64†
Heat of Vaporization (kJ/mol at nbp):	23.9
Source:	No commercial source was identified.
Price:	na

Toxicity: No toxicity information was identified for this compound. By analogy with other phosphorous halides it is very likely that it would be assigned a HR rating of 3 using the Sax and Lewis (high toxic, fire, or reactivity hazard) system.

Sax, N.I. and Lewis, Sr., R.J., Dangerous Properties of Industrial Materials, 7 Ed., Van Nostrand Reinhold, New York, 1989.

Comments: This compound is included on the list to test mechanisms for fire suppression. It is a dangerous and unstable species. Particular care must be exercised in its synthesis and testing.

A standard preparative procedure is available in the literature.

Morse, J.G., Cohn, K., Rudolph, R.W., and Parry, R.W., "3B Phosphorous. 22. Substituted Difluoro- and Dichlorophosphines," Inorganic Syntheses, vol. 10, pp. 147-156, 1967.

No fire suppression measurements were identified for this compound.

†Estimated for this report by authors, na = not available

Name: phosphoryl fluoride

Compound group:	phosphorus-containing compounds
Formula:	POF_3
Alternate Names:	
CASN:	13478-20-1
Normal boiling point (nbp °C):	-40
Vapor pressure (atm at 298 K):	13.2
Heat capacity (J/K-mol at 298 K):	68.8
Heat of Vaporization (kJ/mol at nbp):	22.1
Source:	Atomergic Chemetals Corporation, Plainview, NY 11803, 516-349-8800
Price:	$400/200 g

Toxicity: No toxicity information was identified for this compound. By analogy with other phosphoryl halides it is very likely that it would be assigned a HR rating of 3 using the Sax and Lewis (high toxic, fire, or reactivity hazard) system.

Sax, N.I. and Lewis, Sr., R.J., Dangerous Properties of Industrial Materials, 7 Ed., Van Nostrand Reinhold, New York, 1989.

Comments: No fire suppression measurements were identified for this compound.

Name: phosphoryl chloride

Compound group:	phosphorus-containing compounds
Formula:	$POCl_3$
Alternate Names:	phosphorus oxychloride, phosphorous oxytrichloride

CASN:	10025-87-3
Normal boiling point (nbp °C):	106
Vapor pressure (atm at 298 K):	0.05
Heat capacity (J/K-mol at 298 K):	84.9
Heat of Vaporization (kJ/mol at nbp):	33.7
Source:	Aldrich Chemical Company, Milwaukee, WI, 53233, 800-558-9160
Price:	$207.05/100 g

Toxicity: Sax and Lewis: HR:3, High toxic, fire, or reactivity hazard
Poison by inhalation and ingestion; a corrosive eye, skin, and mucous irritant.

Sax, N.I. and Lewis, Sr., R.J., Dangerous Properties of Industrial Materials, 7th Ed., Van Nostrand Reinhold, New York, 1989.

Comments: Fire suppression references:

Miller, W.J., "Inhibition of Low Pressure Flames," Combustion and Flame, vol. 13, pp. 210-212, April 1969.

Jorissen, W.P., Booy, J., and van Heiningen, J., "Reaction-Regions XXII. On the Prevention of Explosive Reactions in Gas and Vapour Mixtures by Small Amounts of Various Substances," Recueil des Travaux Chimiques des Pay-Bas, vol. 51, pp. 868-877, 15 July 1932.

Name: phosphoryl bromide fluoride

Compound group:	phosphorus-containing compounds
Formula:	POF_2Br
Alternate Names:	

CASN:	14014-18-7
Normal boiling point (nbp °C):	32
Vapor pressure (atm at 298 K):	0.77
Heat capacity (J/K-mol at 298 K):	$75^{\dagger}$
Heat of Vaporization (kJ/mol at nbp):	29.7
Source:	No commercial source was identified.
Price:	na

Toxicity: No toxicity information was identified for this compound. By analogy with other phosphoryl halides it is very likely that it would be assigned a HR rating of 3 (high toxic, fire, or reactivity hazard) using the Sax and Lewis system.

Sax, N.I. and Lewis, Sr., R.J., Dangerous Properties of Industrial Materials, 7 Ed., Van Nostrand Reinhold, New York, 1989.

Comments: This compound is included on the list to test mechanisms for fire suppression. It is a dangerous and unstable species. Particular care must be exercised in its synthesis and testing.

A preparative procedure is available in the literature.

Bernstein, P.A., Hohorst, F.A., Eisenberg, M., and DesMarteau, D.D., "Preparation of Pure Difluorophosphoric Acid and μ-Oxo-bis(phosphoryl difluoride)," Inorganic Chemistry, vol. 10, pp. 1549-1551, July 1971.

No fire suppression measurements were identified for this compound.

†Estimated for this report by authors, na - not available

Name: tetrachlorosilane

Compound group:	Silicon and Germanium
Formula:	$SiCl_4$
Alternate Names:	Silicon tetrachloride

CASN:	10026-04-07
Normal boiling point (nbp °C):	58
Vapor pressure (atm at 298 K):	0.31
Heat capacity (J/K-mol at 298 K):	145
Heat of Vaporization (kJ/mol at nbp):	32
Source:	Liquid Carbonic, Corporation, Chicago, IL, 60603, 312-855-2500
Price (per kg):	$11

Toxicity: Sax and Lewis assign a hazard rating of 3. (high toxic, fire, explosive, or reactivity hazard).

Sax, N. I. and Lewis, R. J., Dangerous Properties of Industrial Materials, Seventh Edition, Van Nostrand Reinhold, New York, 1989.

Comments: Fire suppression references:

"Final Report on Fire Extinguishing Agents for the Period September 1, 1947 to June 30, 1950," Purdue Research Foundation and Department of Chemistry, Purdue University, West Lafayette, IN, July 1950.

Lask, G. and Wagner, H. Gg., "Influence of Additives on the Velocity of Laminar Flames," Eighth Symposium (International) on Combustion, pp. 432-438, Williams and Wilkins, Baltimore, 1962.

Morrison, M. E. and Scheller, K., "The Effect of Burning Velocity Inhibitors on the Ignition of Hydrocarbon-Oxygen-Nitrogen Mixtures," Combustion and Flame, vol. 18, pp. 3-12, 1972.

Name: trichlorofluorosilane

Compound group:	Silicon and Germanium
Formula:	$SiCl_3F$
Alternate Names:	

CASN:	14965-52-77
Normal boiling point (nbp °C):	15
Vapor pressure (atm at 298 K):	1.46
Heat capacity (J/K-mole at 298 K):	92
Heat of Vaporization (kJ/mole at nbp):	26
Source:	No commercial source was identified
Price:	na

Toxicity: High. Halosilanes hydrolyze in moist air - forming hydrogen halides in the process.

Rochow, E. G. in Comprehensive Inorganic Chemistry, vol. 11, Pergamon Press, New York, 1973.

Comments: No fire suppression measurement data was uncovered.

References pertaining to the synthesis of this compound can be found in:

Ebsworth, E. A. V., Volatile Silicon Compounds, Academic Press, New York, NY, 1975.

na = not available.

Name: tetrafluorosilane

Compound group:	Silicon and Germanium
Formula:	SiF_4
Name:	Silicon tetrafluoride

CASN:	7783-61-1
Normal boiling point (nbp °C):	-65
Vapor pressure (atm at 298 K):	1510
Heat capacity (J/K-mol at 298 K):	74
Heat of Vaporization (kJ/mol at nbp):	22
Source:	Liquid Carbonic, Corporation, Chicago, IL, 60603, 312-855-2500
Price (per kg):	$250

Toxicity: Sax and Lewis assign a hazard rating of 3 (high toxic, fire, explosive, or reactivity hazard).

Sax, N. I. and Lewis, R. J., Dangerous Properties of Industrial Materials, Seventh Edition, Van Nostrand Reinhold, New York, 1989.

Comments: No fire suppression measurement data was uncovered.

Name: bromotrifluorosilane

Compound group:	Silicon and Germanium
Formula:	$SiBrF_3$
Alternate Names:	
CASN:	14049-39-9
Normal boiling point (nbp °C):	-42
Vapor pressure (atm at 298 K):	10.5
Heat capacity (J/K-mol at 298 K):	80†
Heat of Vaporization (kJ/mol at nbp):	18
Source:	No commercial source was identified
Price (per kg):	na

Toxicity: High. Halosilanes have a tendency to hydrolyze in moist air - forming hydrogen halides in the process.

Rochow, E. G. in Comprehensive Inorganic Chemistry, vol. 11, Pergamon Press, New York, 1973.

Comments: No fire suppression measurement data was uncovered.

References pertaining to the synthesis of this compound can be found in:

Ebsworth, E. A. V., Volatile Silicon Compounds, Academic Press, New York, NY, 1975.

†Estimated for this report by authors, na = not available

Name: tribromofluorosilane

Compound group:	Silicon and Germanium
Formula:	$SiBr_3F$
Alternate Names:	
CASN:	18356-67-7
Normal boiling point (nbp °C):	84
Vapor pressure (atm at 298 K):	0.11
Heat capacity (J/K-mol at 298):	150[†]
Heat of Vaporization (kJ/mole at nbp):	34
Source:	No commercial source was identified
Price (per kg):	na

Toxicity: High. Halosilanes have a tendency to hydrolyze in moist air - forming hydrogen halides in the process.

Rochow, E. G. in Comprehensive Inorganic Chemistry, vol. 11, Pergamon Press, New York, 1973.

Comments: No fire suppression measurement data were uncovered. References pertaining to the synthesis of this compound can be found in:

Ebsworth, E. A. V., Volatile Silicon Compounds, Academic Press, New York, NY, 1975.

[†] Estimated for this report by authors, na = not available

Name: tetramethylsilane

Compound group:	Silicon and Germanium
Formula:	$Si(CH_3)_4$
Alternate Names:	TMS

CASN:	75-76-3
Normal boiling point (nbp °C):	27
Vapor pressure (atm at 298 K):	0.95
Heat capacity (J/K-mol at 298 K):	204
Heat of Vaporization (kJ/mole at nbp):	27
Source:	Aldrich Chemical Company, Milwaukee, WI, 53233, 800-558-9160
Price (per kg):	$185

Toxicity: High.

The Sigma-Aldrich Library of Chemical Safety Data, First Edition (Lenga, R. E., Editor), Sigma-Aldrich, 1985.

Comments: Fire suppression references:

Lask, G. and Wagner, H. Gg., "Influence of Additives on the Velocity of Laminar Flames," Eighth Symposium (International) on Combustion, pp. 432-438, Williams and Wilkins, Baltimore, 1962.

Morrison, M. E. and Scheller, K., "The Effect of Burning Velocity Inhibitors on the Ignition of Hydrocarbon-Oxygen-Nitrogen Mixtures," Combustion and Flame, vol. 18, pp. 3-12, 1972.

Name: chlorotrimethylsilane

Compound group:	Silicon and Germanium
Formula:	$Si(CH_3)_3Cl$
Alternate Names:	
CASN:	75-77-4
Normal boiling point (nbp °C):	57
Vapor pressure (atm at 298 K):	0.31
Heat capacity (J/K-mol at 298 K):	175†
Heat of Vaporization (kJ/mol at nbp):	32
Source:	Aldrich Chemical Company, Milwaukee, WI, 53233, 800-558-9160
Price (per kg):	$39

Toxicity: Sax and Lewis assign a hazard rating of 3 (high toxic, fire, explosive, or reactivity hazard).

Sax, N. I. and Lewis, R. J., Dangerous Properties of Industrial Materials, Seventh Edition, Van Nostrand Reinhold, New York, 1989.

Comments: No fire suppression measurement data was uncovered.

†Estimated for this report by authors

Name: trichloromethylsilane

Compound group:	Silicon and Germanium
Formula:	$Si(CH_3)Cl_3$
Alternate Names:	
CASN:	75-79-6
Normal boiling point (nbp °C):	66
Vapor pressure (atm at 298 K):	0.23
Heat capacity (J/K-mol at 298 K):	100†
Heat of Vaporization (kJ/mol at nbp):	31
Source:	Aldrich Chemical Company, Milwaukee, WI, 53233, 800-558-9160
Price (per kg):	$29

Toxicity: Sax and Lewis assign a hazard rating of 3 (high toxic, fire, explosive, or reactivity hazard).

Sax, N. I. and Lewis, R. J., Dangerous Properties of Industrial Materials, Seventh Edition, Van Nostrand Reinhold, New York, 1989.

Comments: No fire suppression measurement data was uncovered.

†Estimated for this report by authors

Name: chloromethyltrimethylsilane

Compound group:	Silicon and Germanium
Formula:	$Si(CH_3)CH_2Cl$
Alternate Names:	
CASN:	2344-80-1
Normal boiling point (nbp °C):	98
Vapor pressure (atm at 298 K):	na
Heat capacity (J/K-mol at 298 K):	200†
Heat of Vaporization (kJ/mol at nbp):	na
Source:	Aldrich Chemical Company, Milwaukee, WI, 53233, 800-558-9160
Price (per kg):	$1246

Toxicity: High.

The Sigma-Aldrich Library of Chemical Safety Data, First Edition (Lenga, R. E., Editor), Sigma-Aldrich, 1985.

Comments: No fire suppression measurement data was uncovered.

†Estimated for this report by authors, na = not available.

Name: tetrachlorogermane

Compound group:	Silicon and Germanium
Formula:	$GeCl_4$
Alternate Names:	Germanium tetrachloride

CASN:	10038-98-9
Normal boiling point (nbp °C):	83
Vapor pressure (atm at 298 K):	0.11
Heat capacity (J/K-mol at 298 K):	150†
Heat of Vaporization (kJ/mol at nbp):	35
Source:	Aldrich Chemical Company, Milwaukee, WI, 53233, 800-558-9160
Price (per kg):	$1652

Toxicity: Sax and Lewis assign a hazard rating of 3 (high toxic, fire, explosive, or reactivity hazard).

Sax, N. I. and Lewis, R. J., Dangerous Properties of Industrial Materials, Seventh Edition, Van Nostrand Reinhold, New York, 1989.

Comments: Fire suppression references:

Lask, G. and Wagner, H. Gg., "Influence of Additives on the Velocity of Laminar Flames," Eighth Symposium (International) on Combustion, pp. 432-438, Williams and Wilkins, Baltimore, 1962.

Morrison, M. E. and Scheller, K., "The Effect of Burning Velocity Inhibitors on the Ignition of Hydrocarbon-Oxygen-Nitrogen Mixtures," Combustion and Flame, vol. 18, pp. 3-12, 1972.

†Estimated for this report by authors.

Name: tetramethylgermane

Compound group:	Silicon and Germanium
Formula:	$Ge(CH_3)_4$
Alternate Names:	
CASN:	865-52-1
Normal boiling point (nbp °C):	44
Vapor pressure (atm at 298 K):	0.52
Heat capacity (J/K-mol at 298 K):	200†
Heat of Vaporization (kJ/mole at nbp):	30
Source:	No commercial source was identified
Price (per kg):	na

Toxicity: No information on the toxicity of this specific chemical was found. However, related compounds are not particularly toxic.

Sax, N. I. and Lewis, R. J., Dangerous Properties of Industrial Materials, Seventh Edition, Van Nostrand Reinhold, New York, 1989.

Comments: No fire suppression data have been reported for this compound.

References pertaining to the synthesis of this compound can be found in:

Glockling, F., The Chemistry of Germanium, Academic Press, New york, NY, 1969.

†Estimated for this report by authors, na = not available.

Name: sodium hydrogen carbonate

Compound group:	Metallic
Formula:	$NaHCO_3$
Alternate Names:	Sodium bicarbonate

CASN:	144-55-8
Normal boiling point (nbp °C):	decomposes
Vapor pressure (atm at 298 K):	$0^{\dagger}$
Heat capacity (J/K-mol at 298 K):	88
Heat of vaporization (kJ/mol at nbp):	na
Source:	Aldrich Chemical Company, Milwaukee, WI, 53233, 800-558-9160
Price (per kg):	$16

Toxicity: Low. Sax and Lewis assign a hazard rating of 1.

Sax, N. I. and Lewis, R. J., Dangerous Properties of Industrial Materials, Seventh Edition, Van Nostrand Reinhold, New York, 1989.

Comments: Fire suppression references:

Birchall, J. D., "On the Mechanism of Flame Inhibition by Alkali Metal Salts," Combustion and Flame, vol. 14, pp 85-96, 1970.

Friedman, R. and Levy, J. B., "Inhibition of Opposed - Jet Methane - Air Diffusion Flames. The Effects of Alkali Metal Vapors and Organic Halides," Combustion and Flame, vol. 7, pp. 195-201, 1963.

†Estimated for this report by authors, na = not available.

Name: sodium acetate

Compound group:	Metallic
Formula:	$NaC_2H_3O_2$
Alternate Names:	Acetic acid, sodium salt

CASN:	127-09-3
Normal boiling point (nbp °C):	decomposes
Vapor pressure (atm at 298 K):	0†
Heat capacity (J/K-mol at 298 K):	80
Heat of vaporization (kJ/mol at nbp):	na
Source:	Aldrich Chemical Company, Milwaukee, WI, 53233, 800-558-9160
Price:	$36 (per kg)

Toxicity: Medium. Sax and Lewis assign a hazard rating of 2.

Sax, N. I. and Lewis, R. J., Dangerous Properties of Industrial Materials, Seventh Edition, Van Nostrand Reinhold, New York, 1989.

Comments: Fire suppression references:

Dewitte, M., Vrebosch, J. and van Tiggelen, A., "Inhibition and Extinction of Premixed Flames by Dust Particles," Combustion and Flame, vol. 8, pp. 257-266, 1964.

†Estimated for this report by authors, na = not available.

Name: potassium hydrogen carbonate

Compound group: Metallic
Formula: $KHCO_3$
Alternate Names: Potassium bicarbonate

CASN: 298-14-6
Normal boiling point (nbp °C): decomposes
Vapor pressure (atm at 298 K): $0^{\dagger}$
Heat capacity (J/K-mol at 298 K): na
Heat of vaporization (kJ/mol at nbp): na
Source: Aldrich Chemical Company, Milwaukee, WI, 53233, 800-558-9160
Price (per kg): $24

Toxicity: Low.

Comments: Fire suppression references:

Birchall, J. D., "On the Mechanism of Flame Inhibition by Alkali Metal Salts," Combustion and Flame, vol. 14, pp 85-96, 1970.

Friedman, R. and Levy, J. B., "Inhibition of Opposed - Jet Methane - Air Diffusion Flames. The Effects of Alkali Metal Vapors and Organic Halides," Combustion and Flame, vol. 7, pp. 195-201, 1963.

†Estimated for this report by author, na = not available.

Name: potassium oxalate

Compound group:	Metallic
Formula:	$K_2C_2O_4 \bullet H_2O$
Alternate Names:	Potassium oxalate monohydrate

CASN:	6487-48-5
Normal boiling point (nbp °C):	decomposes
Vapor pressure (atm at 298 K):	$0^\dagger$
Heat capacity (J/K-mol at 298 K):	na
Heat of vaporization (kJ/mol at nbp):	na
Source:	Aldrich Chemical Company, Milwaukee, WI, 53233, 800-558-9160
Price (per kg):	$46

Toxicity: Sax and Lewis assign a hazard rating of 3. (high toxic, fire, explosive, or reactivity hazard).

Sax, N. I. and Lewis, R. J., Dangerous Properties of Industrial Materials, Seventh Edition, Van Nostrand Reinhold, New York, 1989.

Comments: Fire suppression references:

Friedrich, M. "Extinguishment Action of Powders," Fire Research Abstracts and Reviews, vol. 2, pp. 132-135, 1960.

Dewitte, M., Vrebosch, J. and van Tiggelen, A., "Inhibition and Extinction of Premixed Flames by Dust Particles," Combustion and Flame, vol. 8, pp. 257-266, 1964.

†Estimated for this report by authors, na = not available.

Name: potassium acetate

Compound group:	Metallic
Formula:	$K_2C_2H_5O_2$
Alternate Names:	Acetic acid, potassium salt
CASN:	127-08-2
Normal boiling point (nbp °C):	decomposes
Vapor pressure (atm at 298 K):	$0^\dagger$
Heat capacity (J/K-mol at 298 K):	na
Heat of vaporization (kJ/mol at nbp):	na
Source:	Aldrich Chemical Company, Milwaukee, WI, 53233, 800-558-9160
Price (per kg):	$39

Toxicity: Medium. Sax and Lewis assign a hazard rating of 2.

Sax, N. I. and Lewis, R. J., Dangerous Properties of Industrial Materials, Seventh Edition, Van Nostrand Reinhold, New York, 1989.

Comments: Fire suppression references:

Dewitte, M., Vrebosch, J. and van Tiggelen, A., "Inhibition and Extinction of Premixed Flames by Dust Particles," Combustion and Flame, vol. 8, pp. 257-266, 1964.

†Estimated for this report by authors, na = not available.

Name: potassium acetylacetonate

Compound group:	Metallic
Formula:	$KC_5H_7O_2\bullet\frac{1}{2}H_2O$
Alternate Names:	Potassium acetylacetonate hemihydrate
CASN:	57402-46-7
Normal boiling point (nbp °C):	decomposes
Vapor pressure (atm at 298 K):	na
Heat capacity (J/K-mol at 298 K):	na
Heat of vaporization (kJ/mol at nbp):	na
Source:	Aldrich Chemical Company, Milwaukee, WI, 53233, 800-558-9160
Price (per kg):	$300

Toxicity: High.

Comments: No fire suppression measurement data were uncovered.

na = not available

Name: chromium acetylacetonate

Compound group: Metallic
Formula: $Cr(C_5H_7O_2)_3$
Alternate Names:

CASN: 21679-31-2
Normal boiling point (nbp °C): 340
Vapor pressure (atm at 298 K): na
Heat capacity (J/K-mol at 298 K): na
Heat of vaporization (kJ/mol at nbp): na
Source: Aldrich Chemical Company, Milwaukee, WI, 53233, 800-558-9160
Price (per kg): $120

Toxicity: High.

Comments: Fire suppression references:

Vanpee, M. and Shirodkar, P. P., "A Study of Flame Inhibition by Metal Compounds," <u>Seventeenth Symposium (International) in Combustion</u>, pp 787-793, 1978.

na = not available.

Name: chromyl chloride

Compound group:	Metallic
Formula:	CrO_2Cl_2
Alternate Names:	
CASN:	14977-61-8
Normal boiling point (nbp °C):	116
Vapor pressure (atm at 298 K):	0.024
Heat capacity (J/K-mol at 298 K):	na
Heat of vaporization (kJ/mol at nbp):	41
Source:	Aldrich Chemical Company, Milwaukee, WI, 53233, 800-558-9160
Price (per kg):	$2216

Toxicity: Sax and Lewis assign a hazard rating of 3. (high toxic, fire, explosive, or reactivity hazard).

Sax, N. I. and Lewis, R. J., Dangerous Properties of Industrial Materials, Seventh Edition, Van Nostrand Reinhold, New York, 1989.

Comments: Fire suppression references:

Lask, G. and Wagner, H. Gg., "Influence of Additives on the Velocity of Laminar Flames," Eighth Symposium (International) on Combustion, pp. 432-438, Williams and Wilkins, Baltimore, 1962.

Morrison, M. E. and Scheller, K., "The Effect of Burning Velocity Inhibitors on the Ignition of Hydrocarbon-Oxygen-Nitrogen Mixtures," Combustion and Flame, vol. 18, pp. 3-12, 1972.

na = not available.

Name: tin (IV) chloride

Compound group:	Metallic
Formula:	$SnCl_4$
Alternate Names:	Stannic chloride

CASN:	7646-78-8
Normal boiling point (nbp °C):	114
Vapor pressure (atm at 298 K):	0.030
Heat capacity (J/K-mol at 298 K):	165
Heat of vaporization (kJ/mol at nbp):	37
Source:	Aldrich Chemical Company, Milwaukee, WI, 53233, 800-558-9160
Price (per kg):	$45

Toxicity: Sax and Lewis assign a hazard rating of 3. (high toxic, fire, explosive, or reactivity hazard).

Sax, N. I. and Lewis, R. J., Dangerous Properties of Industrial Materials, Seventh Edition, Van Nostrand Reinhold, New York, 1989.

Comments: Fire suppression references:

Lask, G. and Wagner, H. Gg., "Influence of Additives on the Velocity of Laminar Flames," Eighth Symposium (International) on Combustion, pp. 432-438, Williams and Wilkins, Baltimore, 1962.

Morrison, M. E. and Scheller, K., "The Effect of Burning Velocity Inhibitors on the Ignition of Hydrocarbon-Oxygen-Nitrogen Mixtures," Combustion and Flame, vol. 18, pp. 3-12, 1972.

Name: titanium (IV) chloride

Compound group:	Metallic
Formula:	$TiCl_4$
Alternate Names:	
CASN:	7550-45-0
Normal boiling point (nbp °C):	136
Vapor pressure (atm at 298 K):	0.015
Heat capacity (J/K-mol at 298 K):	145
Heat of vaporization (kJ/mol at nbp):	39
Source:	Aldrich Chemical Company, Milwaukee, WI, 53233, 800-558-9160
Price (per kg):	$40

Toxicity: Sax and Lewis assign a hazard rating of 3. (high toxic, fire, explosive, or reactivity hazard).

Sax, N. I. and Lewis, R. J., Dangerous Properties of Industrial Materials, Seventh Edition, Van Nostrand Reinhold, New York, 1989.

Comments: Fire suppression references:

Lask, G. and Wagner, H. Gg., "Influence of Additives on the Velocity of Laminar Flames," Eighth Symposium (International) on Combustion, pp. 432-438, Williams and Wilkins, Baltimore, 1962.

Morrison, M. E. and Scheller, K., "The Effect of Burning Velocity Inhibitors on the Ignition of Hydrocarbon-Oxygen-Nitrogen Mixtures," Combustion and Flame, vol. 18, pp. 3-12, 1972.

Name: tetraethyl lead

Compound group:	Metallic
Formula:	$Pb(C_2H_5)_4$
Alternate Names:	

CASN:	78-00-2
Normal boiling point (nbp °C):	200
Vapor pressure (atm at 298 K):	0.00055
Heat capacity (J/K-mol at 298 K):	na
Heat of vaporization (kJ/mol at nbp):	54
Source:	Alfa Products, Danvers, MA, 01923, 800-342-0660
Price (per kg):	$15500

Toxicity: Sax and Lewis assign a hazard rating of 3. (high toxic, fire, explosive, or reactivity hazard).

Sax, N. I. and Lewis, R. J., Dangerous Properties of Industrial Materials, Seventh Edition, Van Nostrand Reinhold, New York, 1989.

Comments: Fire suppression references:

Lask, G. and Wagner, H. Gg., "Influence of Additives on the Velocity of Laminar Flames," Eighth Symposium (International) on Combustion, pp. 432-438, Williams and Wilkins, Baltimore, 1962.

Morrison, M. E. and Scheller, K., "The Effect of Burning Velocity Inhibitors on the Ignition of Hydrocarbon-Oxygen-Nitrogen Mixtures," Combustion and Flame, vol. 18, pp. 3-12, 1972.

na = not available

Name: iron pentacarbonyl

Compound group:	Metallic
Formula:	$Fe(CO)_5$
Alternate Names:	Iron carbonyl
CASN:	13463-40-6
Normal boiling point (nbp °C):	103
Vapor pressure (atm at 298 K):	0.040
Heat capacity (J/K-mol at 298 K):	241
Heat of vaporization (kJ/mol at nbp):	38
Source:	Aldrich Chemical Company, Milwaukee, WI, 53233, 800-558-9160
Price (per kg):	$79

Toxicity: Sax and Lewis assign a hazard rating of 3. (high toxic, fire, explosive, or reactivity hazard).

Sax, N. I. and Lewis, R. J., Dangerous Properties of Industrial Materials, Seventh Edition, Van Nostrand Reinhold, New York, 1989.

Comments: Fire suppression data references:

Lask, G. and Wagner, H. Gg., "Influence of Additives on the Velocity of Laminar Flames," Eighth Symposium (International) on Combustion, pp. 432-438, Williams and Wilkins, Baltimore, 1962.

Morrison, M. E. and Scheller, K., "The Effect of Burning Velocity Inhibitors on the Ignition of Hydrocarbon-Oxygen-Nitrogen Mixtures," Combustion and Flame, vol. 18, pp. 3-12, 1972.

Vanpee, M. and Shirodkar, P. P., "A Study of Flame Inhibition by Metal Compounds," Seventeenth Symposium (International) in Combustion, pp 787-793, 1978.

Name: nitrogen

Compound group:	inert gases
Formula:	N_2
Alternate Names:	
CASN:	7727-37-9
Normal boiling point (nbp °C):	-195.8
Vapor pressure (atm at 298 K):	na
Heat capacity (J/K-mol at 298 K):	29.3
Heat of Vaporization (kJ/mol at nbp):	5.6
Source:.	Matheson Gas Products, Baltimore, MD 21227, 301-796-0517
Price:	(99.998%) $42/8.3 kg

Toxicity: Sax and Lewis: HR:1, low toxic, fire, or reactivity hazard.
Low toxicity; in high concentrations it is a simple asphyxiant.

Comments: The effects of nitrogen on flames have been investigated extensively. A few representative references are provided.

Coward, H.F. and Hartwell, F.J., "Extinction of Methane Flames by Diluent Gases," Journal of the Chemical Society, pp. 1522-1532, 1926.

Simmons, R.F. and Wolfhard, H.G., "Some Limiting Oxygen Concentrations for Diffusion Flames in Air Diluted with Nitrogen," Combustion and Flame, vol. 1, pp. 155-161, 1957.

Tatem, P.A., Gann, R.G., and Carhart, H.W., "Pressurization with Nitrogen as an Extinguishant for Fires in Confined Spaces," Combustion Science and Technology, vol. 7, pp. 213-218, 1973.

Ishizuka, S. and Tsuji, H., "An Experimental Study of Effect of Inert Gases on Extinction of Laminar Diffusion Flames," Eighteenth Symposium (International) on Combustion, pp. 695-703, The Combustion Institute, Pittsburgh, 1981.

Tucker, D.M., Drysdale, D.D., and Rasbash, D.J., "The Extinction of Diffusion Flames Burning in Various Oxygen Concentration by Inert Gases and Bromotrifluormethane," Combustion and Flame, vol. 41, pp. 292-300, 1981.

na = not available.

Name: carbon dioxide

Compound group: inert gases
Formula: CO_2
Alternate Names:

CASN: 124-38-9
Normal boiling point (nbp °C): -75.8 (sublimes)
Vapor pressure (atm at 298 K): 29.9
Heat capacity (J/K-mol at 298 K): 37.7
Heat of Vaporization (kJ/mol at nbp): 15.3
Source: Matheson Gas Products, Baltimore, MD 21227, 301-796-0517
Price: (99.99%) $95/27.2 kg

Toxicity: Sax and Lewis: HR:1, Low toxic, fire, or reactivity hazard
An asphyxiant; an experimental teratogen.

Comments: The effects of carbon dioxide on flames have been investigated extensively. A few representative references are provided.

Coward, H.F. and Hartwell, F.J., "Extinction of Methane Flames by Diluent Gases," Journal of the Chemical Society, pp. 1522-1532, 1926.

Egerton, A. and Powling, J., "The Limits of Flame Propagation at Atmospheric Pressure. II. The Influence of Changes in the Physical Properties," Proceedings of the Royal Society of London, vol. A197, pp. 190-209, May 27, 1948.

Tucker, D.M., Drysdale, D.D., and Rasbash, D.J., "The Extinction of Diffusion Flames Burning in Various Oxygen Concentration by Inert Gases and Bromotrifluormethane," Combustion and Flame, vol. 41, pp. 292-300, 1981.

Name: argon

Compound group:	inert gases
Formula:	Ar
Alternate Names:	

CASN:	7440-37-1
Normal boiling point (nbp °C):	-185.4
Vapor pressure (atm at 298 K):	na
Heat capacity (J/K-mol at 298 K):	20.9
Heat of Vaporization (kJ/mol at nbp):	6.5
Source:	Matheson Gas Products, Baltimore, MD 21227, 301-796-0517
Price:	(99.998%) $77/13.5 kg

Toxicity: Sax and Lewis: HR:1, low toxic, fire, or reactivity hazard
A simple asphyxiant gas.

Comments: The effects of argon on flames have been investigated extensively. A few representative references are provided.

Coward, H.F. and Hartwell, F.J., "Extinction of Methane Flames by Diluent Gases," Journal of the Chemical Society, pp. 1522-1532, 1926.

Egerton, A. and Powling, J., "The Limits of Flame Propagation at Atmospheric Pressure. II. The Influence of Changes in the Physical Properties," Proceedings of the Royal Society of London, vol. A197, pp. 190-209, May 27, 1948.

Ishizuka, S. and Tsuji, H., "An Experimental Study of Effect of Inert Gases on Extinction of Laminar Diffusion Flames," Eighteenth Symposium (International) on Combustion, pp. 695-703, The Combustion Institute, Pittsburgh, 1981.

na = not available.

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11. ABSTRACT (A 200-WORD OR LESS FACTUAL SUMMARY OF MOST SIGNIFICANT INFORMATION. IF DOCUMENT INCLUDES A SIGNIFICANT BIBLIOGRAPHY OR LITERATURE SURVEY, MENTION IT HERE.)

Production of the currently-used halogenated fire suppressants (halons) will be curtailed because of their contribution to stratospheric ozone depletion. This report, one of the first efforts toward identifying alternatives, documents the rationale for and selection of a set of approximately one hundred gases and/or liquids, covering a range of chemical and physical principles thought to affect flame suppression capability and stratospheric ozone depletion. An Appendix provides extensive information on each of the selected chemicals. Also included in the report are an introduction to combustion concepts, fire suppression mechanisms, test approaches for flame suppression effectiveness, and the mechanisms by which the current commercial halons can decrease stratospheric ozone.

12. KEY WORDS (6 TO 12 ENTRIES; ALPHABETICAL ORDER; CAPITALIZE ONLY PROPER NAMES; AND SEPARATE KEY WORDS BY SEMICOLONS)

fire suppression; halons

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