NMERI 97/6/33010

IDENTIFICATION AND PROOF TESTING OF NEW TOTAL FLOODING AGENTS: COMBUSTION SUPPRESSION CHEMISTRY AND CUP-BURNER TESTING

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Final Report, February 1997 - February 1998

May 1998

Sponsored by:

U. S. Department of Defense
Strategic Environmental Research and Development Program

NOTICE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE
13 June 1998

3. REPORT TYPE AND DATES COVERED
Final Report, 3 Feb. 1997 - 2 Feb. 1998

4. TITLE AND SUBTITLE
Identification and Proof Testing of New Total Flooding Agents: Combustion Suppression Chemistry and Cup-Burner Testing

5. FUNDING NUMBERS
C MDA972-97-M-0011

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
New Mexico Engineering Research Institute
The University of New Mexico
Albuquerque, New Mexico 87106-4339

8. PERFORMING ORGANIZATION REPORT NUMBER
NMERI 97/6/33010

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Department of Defense, Strategic Environmental Research and Development Program

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11 SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Under the Montreal Protocol, an international treaty, the production of the fire and explosion protection agent Halon 1301 (bromotrifluoromethane, BFC-13B1, $CBrF_3$) was phased out in the U. S. at the end of 1993. To date, no environmentally acceptable halon substitute equivalent to the existing halons in toxicity, effectiveness, and dimensionality has been identified. The objectives of the overall effort is to reassess the higher volatility chemicals in the families of phosphorus nitrides, silanes, siloxanes, fluorinated amines and/or ethers, and other non-halocarbons which might be appropriate for Halon 1301 replacement applications. In an accompanying report (Tapscott, R. E., Heinonen, E. W., and Mather, J. D., *Identification and Proof Testing of New Total Flooding Agents: Toxicity and Global Environmental Assessment*, NMERI 97/29/33010, U. S.DoD Strategic Environmental Research and Development Program and the Defense Advance Research Projects Agency—Arlington, VA, February 1998), the toxicities, Ozone Depletion Potentials,and Global Warming Potentials were examined. The present report examines the chemistry and flame extinguishment characteristics of the materials. A list of compounds for further study is presented.

14. SUBJECT TERMS
halon; fire extinguishment; cup burner; phosphorus; amines; silicon; ethers

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
UNCLASSIFIED

18. SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT
Unclassified

20. LIMITATION OF ABSTRACT
Unclassified

NSN 7540-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std 239-18

PREFACE

This report was prepared by the Center for Global Environmental Technologies (CGET) Division, New Mexico Engineering Research Institute (NMERI), The University of New Mexico, Albuquerque, New Mexico, for the U.S. Department of Defense, Strategic Environmental Research and Development Program, under Contract MDA972-97-M-0011, NMERI Number 8-33010.

The Start Date was 3 February 1997, and the End Date was 2 February 1998. The Technical Program Manager is Dr. Richard G. Gann, National Institute of Standards and Technology; the Contracting Officer's Technical Representative (COTR) is Dr. Andrzej W. Miziolek, Army Research Laboratory, and the NMERI Principal Investigator is Dr. Robert E. Tapscott.

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SUMMARY

A. TASK OBJECTIVES

The objective of the overall effort is to reassess the higher volatility chemicals in the families of phosphorus nitrides, silanes, siloxanes, fluorinated amines and/or ethers, and other nonhalocarbons, which might be appropriate for Halon 1301 replacement applications.

B. TECHNICAL PROBLEMS

Many of the compounds believed to contain favorable environmental, toxicological, and potentially acceptable performance characteristics are difficult to synthesize and are as a result not immediately available for testing. Potential sources and synthetic routes to some of these materials have, however, been determined. In many but not all cases, basic physical properties (boiling point and vapor pressure, for example), toxicities, and environmental values (ozone depletion potentials and global warming potentials) are likewise not available. On the other hand, relatively reliable estimates of the environmental properties have been determined and are presented in an accompanying report (*Identification and Proof Testing of New Total Flooding Agents: Toxicity and Global Environmental Assessment, Interim Report*, Tapscott, R. E., Heinonen, E. W., and Mather, J. D., NMERI 97/29/33010, U. S. DoD Strategic Environmental Research and Development Program and the Defense Advance Research Projects Agency, Arlington, VA, February 1998).

C. GENERAL METHODOLOGY

This project involves the four tasks described below:

1. The toxicities, Ozone Depletion Potentials (ODP), and Global Warming Potentials (GWP) of phosphorus nitrides, silanes, siloxanes, fluorinated amines and/or ethers, and other nonhalocarbons that might be appropriate for Halon 1301 applications will be estimated. Estimation techniques will include Quantitative Structure Activity Relationships (QSAR) for toxicity; estimated or known hydroxyl free radical rate constants with globally averaged atmospheric hydroxyl radical concentrations for

lifetimes; estimation methods for conversion of lifetimes to ODP and GWP based on data fitting to known values; and estimation of physical removal and photolytic removal based on chemical and physical properties.

2. Specific compounds will be selected for study based on the information obtained in Task 1. Compounds not readily available will be synthesized. To the extent practical, quantities of synthesized compounds sufficient to permit other researchers to examine the materials will be prepared.
3. Cup-burner flame extinguishment evaluations will be performed using the New Mexico Engineering Research Institute (NMERI) Standard Cup Burner.
4. The information obtained in the above tasks will be assessed to develop a list of optimal candidate Halon 1301 replacement agents. The criteria for this list will be based primarily on (1) predicted toxicity, (2) synthesis and manufacturability, (3) ODP and GWP, and (4) fire suppression and inertion effectiveness.

D. TECHNICAL RESULTS

New identified chemistry and extinguishment data to supplement information in past reports have been provided for phosphorus compounds, silicon compounds, amines, and fluoroethers.

Syntheses were attempted on some compounds, and cup-burner testing was attempted on 12 compounds. In several cases, however, compound volatility was too low to permit testing or, at least, to obtain reliable results.

Nineteen (19) phosphorus compounds, silicon compounds, amines, and fluoroethers are recommended for further study.

E. IMPORTANT FINDINGS AND CONCLUSIONS

Of the families examined, phosphorus compounds provide the most promising candidates for continued work. Of particular importance is the relatively low *n*-heptane cup-burner extinguishment concentration of 2.4 vol.% found for tris(2,2,2-trifluoroethyl)phosphite ($P(OCH_2CF_3)_3$). Phosphines provide good materials for mechanistic studies; however, phosphines can be ruled out as candidates owing to their inherent low stability (many are flammable, sometimes spontaneously, even with fluorinated substituents) and high toxicities. Though it is possible to obtain fire extinguishment (sometimes, very good) with phosphazenes, these compounds have an inherently high molecular weight and, therefore, very low volatility. Of the phosphorus compounds, the esters of phosphorus-containing acids are the most promising candidates.

The primary problems of phosphorus-containing esters are their often high boiling points and viscosities and the flammability of many of the materials. Fluorination would, of course, aid in all of these problems. The most promising compounds are phosphites with formulas such as $P(OR_f)_3$, where R_f is a fluorinated group, which should have as low a molecular weight and as high a fluorination as possible. Tris(trifluoromethyl)phosphite ($P(OCF_3)_3$), if it can be made, is an ideal compound for evaluation. Others of particular interest are phosphites containing mixed $-CF_3$ and $-C_2F_5$ groups and tris(pentafluoroethyl)phosphite ($P(OCF_2CF_3)_3$). The second most promising families are the phosphates with structures similar to those presented above for the phosphites, e.g., tris(trifluoromethyl)phosphate ($O{=}P(OCF_3)_3$) and tris(pentafluoroethyl) phosphate ($O{=}P(OCF_2CF_3)_3$). Finally, phosphites and phosphates with a bromine-containing alkyl group, e.g., (bromodifluoromethyl)bis(trifluoromethyl)phosphite ($P(OCF_3)_2(OCF_2Br)$) and (bromodifluoromethyl)bis(trifluoromethyl)phosphate ($O{=}P(OCF_3)_2(OCF_2Br)$) require investigation. Such compounds are expected to exhibit fire suppression synergism between the bromine and phosphorus.

A major problem is syntheses of phosphate and phosphite esters of the types proposed. Phosphites can be easily synthesized by reaction of PCl_3 with ROH. These, in turn, can be oxidized to the phosphates. Unfortunately, alcohols that could be used to prepare esters containing fluorine bound to the carbon atom adjacent to oxygen are inherently unstable, breaking down by a 1,2-elimination of hydrogen fluoride (HF) to give carbonyl compounds. There may, however, be other means to prepare such esters.

Silicon compounds appear to offer relatively little promise. Silicon offers little inherent fire suppression capability due to the silicon itself, and many of the most interesting compounds (e.g., those containing bromofluoroalkyl and/or fluoroalkyl groups) are difficult to synthesize.

Of particular concern is the instability of compounds containing $-CF_3$ groups immediately adjacent to the silicon atom, and such compounds are not considered here. All of the most promising silicon compounds are likely to have a low volatility and a high viscosity.

Amines, on the other hand, offer significant promise, particularly because a large amount of research is underway in Japan on the applications of fluoroalkyl amines as halon and CFC replacements. Compounds such as $N(CF_3)(CHF_2)(CF_2Br)$ could provide short atmospheric lifetimes and chemical suppression.

A large amount of research is underway on fluoroethers as CFC replacements. The ether linkage provides a lower atmospheric lifetime only if it contains some hydrogen atoms. Work here and elsewhere indicates that in the absence of a bromine group, fluorinated ethers offer a fire suppression capability no higher than that of the hydrofluorocarbons and perfluorocarbons. Thus, there is little reason to pursue hydrofluoroethers or perfluoroethers further. Of interest, however, are hydrobromofluoroethers.

F. SIGNIFICANT HARDWARE DEVELOPMENTS

During this project, the NMERI Cup Burner (as reported in “An Update on NMERI Cup-Burner Test Results,” Moore, T. A., Weitz, C. A., and Tapscott, R. E., *Proceedings, Halon Options Technical Working Conference*, Albuquerque, NM, pp. 551-567, May 1996) was modified to use volume delivered by a syringe pump rather than weight to measure agent delivery rates. The use of a syringe pump has been demonstrated to allow cup-burner testing of high boiling point and/or viscous materials, particularly those that are difficult to pass through valves and delivery lines. Because the syringe pump delivery method allows less holdup of agent in lines and requires less storage, this method allows testing of agents available only in limited amounts. Overall, however, the use of weight is still the most accurate and reliable method for testing.

G. SPECIAL COMMENTS

There are no special comments.

H. IMPLICATIONS FOR FURTHER RESEARCH

Of the compounds examined in this project, future work should emphasize phosphites and, secondarily, amines. Of particular importance is the preparation, if possible, of $P(OCF_3)_3$.

TABLE OF CONTENTS

TABLE OF CONTENTS (concluded)

Section Page

LIST OF TABLES

LIST OF ABBREVIATIONS

BCC	Business Communications Company
CCOD	CGET Chemical Options Database
CGET	Center for Global Environmental Technologies
COTR	Contracting Officer’s Technical Representative
DMMP	dimethyl methylphosphonate
GC	gas chromatography
GC/MS	gas chromatography/mass spectrometry
GWP	Global Warming Potential
HFPE	hydrofluoropolyether
HMPA	hexamethylphosphoramide
MSDS	Material Safety Data Sheet
NIRI	National Industrial Research Institute
NMERI	New Mexico Engineering Research Institute
ISO	International Standards Organization
ODP	Ozone Depletion Potential
QSAR	Quantitative Structure-Activity Relationship
RT	retention time
USIC	United States Industry Coalition, Inc.

LIST OF UNITS AND SYMBOLS

cp	centipoise
g/s	grams/second
vol%	percent by gas volume

SECTION I
INTRODUCTION

A. OBJECTIVE

The objective of this effort is to assess the higher volatility chemicals in the families of phosphorus nitrides, silanes, siloxanes, fluorinated amines and/or ethers, and other nonhalocarbons, which that might be appropriate for Halon 1301 replacement applications.

B. SCOPE

The overall project consists of four requirements:

1. From literature citations and previously determined principles, estimate the toxicity, Ozone Depletion Potential (ODP), and Global Warming Potential (GWP) of the chemicals of interest. This phase of the project was completed earlier and results were presented in an interim report (Reference 1).

2. Select specific compounds for study and, for those compounds that are not readily available, prepare sufficient quantities to permit other researchers to examine the materials.

3. Perform cup-burner flame extinguishment evaluations of selected compounds. Be prepared to provide sufficient quantities of these chemicals to other laboratories for testing using opposed-flame burners or similar apparatuses.

4. Using the information obtained in the above tasks, develop a list of optimal candidate Halon 1301 replacement agents based primarily on (1) predicted toxicity, (2) synthesis and manufacturability, (3) ODP and GWP, and (4) fire suppression and inertion effectiveness.

C. APPROACH

The following tasks were accomplished in this phase of the work:

1. Specific compounds were selected for study based on the information obtained in Task 1. Attempts were made to synthesize some compounds not readily available.

2. Cup-burner flame extinguishment evaluations were performed using the New Mexico Engineering Research Institute (NMERI) Cup Burner and *n*-heptane fuel. As normally configured, the NMERI Cup Burner apparatus monitors weight to determine the agent delivery rate (Reference 2); however, owing to the high boiling point of many of the materials examined here, a need to limit agent holdup in lines, and concerns about agent viscosity, a second version of the NMERI Cup Burner, which employs a syringe pump and monitors flow, was developed.

The modification incorporates a syringe pump to inject the liquid directly into the heated chamber, rather than using overpressure to drive the agent into the chamber. Three advantages with such an apparatus are (1) decreased risk of accidental release due to a leaking line or hose break, (2) lower compound requirement, and (3) decreased possibility of agent retention in lines. The last two advantages result from the absence of lines leading to the needle passing into the mixing chamber.

In this revised procedure, a 5-mL syringe is filled with the test compound and connected to the cup burner, and the flow rate is increased until extinguishment is attained. The syringe is then refilled with the test compound, weighed, and placed back into the syringe pump. After discharge for one minute at the syringe-pump setting for extinguishment, the syringe is reweighed, and the flow rates in mass per unit time can be obtained.

Calibration of the syringe pump delivery with perfluorohexane (C_6F_{14}) gave extinguishing concentrations of 4.25, 4.58, 4.93, and 4.74 vol.% (average 4.625 vol.%), similar to the extinguishment concentration of 4.42 vol.% (Reference 2) determined in the same cup burner using the unmodified method.

The two different cup burner apparatuses are referred to in this report as the Standard NMERI Cup Burner and the Modified NMERI Cup Burner.

3. The information obtained in the above tasks were assessed to develop a list of 19 optimal candidate Halon 1301 replacement agents. The criteria for this list are based primarily on (1) predicted toxicity, (2) synthesis and manufacturability, (3) ODP and GWP, and (4) fire suppression and inertion effectiveness.

During this program, scientists in Russia were found to be a potential source for many compounds of interest. The Applied Chemistry Division of the Russian Scientific Center in St. Petersburg was identified as a particularly promising source for low-cost materials. The list of compounds (Table 1) submitted to this organization for consideration for synthesis received a favorable response; however, it was determined, as the work progressed, that many of the compounds requested had undesirable properties (e.g., $P(CF_3)_3$ is pyrophoric). It was, therefore, decided to postpone ordering compounds until the requirements were better defined (possibly in a future project).

TABLE 1. COMPOUNDS FOR POSSIBLE SYNTHESIS IN RUSSIAN FACILITIES.

Formula	Name
Bromofluoroamines	
$(CBrF_2)(CHF_2)_2N$	(bromodifluoromethyl)bis(difluoromethyl)amine
$(CBrF_2)(CF_3)(CH_3)N$	methyl(bromodifluoromethyl)(trifluoromethyl)amine
$(CF_3)_2(CH_2CBrF_2)N$	bis(trifluoromethyl)(2-bromo-2,2-difluoroethyl)amine
$(CBrF_2)(CF_3)_2N$	bis(trifluoromethyl)(bromodifluoromethyl)amine
Silicon Compounds	
$Si(CF_3)_4$	tetrakis(trifluoromethyl)silane
$Si(CF_3)_3(CF_2Br)$	(bromodifluoromethyl)tris(trifluoromethyl)silane
$Si(CF_2CF_3)_4$	tetrakis(pentafluoroethyl)silane
$Si(CF_2CF_3)_3(CF_2CF_2Br)$	(2-bromo-1,1,2,2-tetrafluoroethyl)tris(pentafluoroethyl)silane
$(CF_3CF_2)_3Si\text{-}O\text{-}Si(CF_2CF_3)_3$	hexakis(pentafluoroethyl)disiloxane
$(CF_3CF_2)_3Si\text{-}O\text{-}Si(CF_2CF_3)_2(CF_2CF_2Br)$	(2-bromo-1,1,2,2-tetrafluoroethyl)-pentakis(pentafluoroethyl)disiloxane
Phosphorus Compounds	
$P(CF_3)_3$	tris(trifluoromethyl)phosphine
$P(CF_3)_2(CF_2Br)$	(bromodifluoromethyl)tris(trifluoromethyl)phosphine
$N_3P_3(CF_3)_6$	hexakis(trifluoromethyl)cyclotriphosphazene
$N_3P_3(OCH_2CF_3)_6$	hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene
$(CF_3)_2NP(CF_3)_2$	perfluoro-(dimethylamino)dimethylphosphine
$((CF_3)_2N)_2P(CF_3)$	perfluoro-bis(dimethylamino)methylphosphine
$((CF_3)_2N)_3P$	perfluoro-tris(dimethylamino)phosphine

SECTION II

PHOSPHORUS COMPOUNDS

A review of the chemistry and fire suppression properties of phosphorus compounds has been presented in Reference 3. Except as otherwise stated, all of the information presented here is newly acquired or is an expansion of information contained in that source.

A. FIRE SUPPRESSION

Liquid fire suppressants with halocarbons containing both phosphates and phosphites have been claimed as fire extinguishants (Reference 4). The mixtures are claimed to give significantly increased fire suppression for Class B fires compared to conventional monoammonium phosphate and halons, and for Class A fires compared to Halon 1211. Reference 3 cites a number of additional papers on fire suppression by phosphorus compounds.

1. Flame Suppression Studies

A relatively large amount of work has been performed on flame suppression by phosphorus containing compounds (Reference 3). Despite the fact that much of this work was performed on phosphorus halides such as phosphorus(V) oxychloride ($POCl_3$) and phosphorus trichloride (PCl_3), there is little doubt that phosphorus itself contributes significantly to extinguishment. Thus, for example, $POCl_3$ is about 10 times more effective than an equivalent amount of chlorine (Reference 5). Moreover, trimethyl phosphate ($(O{=}P(OCH_3)_3)$) shows a more pronounced effect on flame velocity than Cl_2 and Br_2 (Reference 6). Phosphate esters are of particular interest as fire suppressants since they are difficult to ignite and will self-extinguish (Reference 7).

An opposed-jet burner apparatus has been used to study the effectiveness of dimethyl methylphosphonate (DMMP, $O{=}P(CH_3)(OCH_3)_2$) (Reference 8). Global extinction strain rates show that introduction of DMMP with an oxidizer gives significant inhibition of non-premixed methane-air flames. DMMP is approximately 40 times more effective than nitrogen on a molar basis, and about 4 times more effective than Halon 1301. The extinction strain rate decreases linearly with the mole fraction of DMMP for loadings up to 1500 ppm. Studies on flat $H_2/O_2/Ar$ flames by molecular beam mass spectrometry indicate that DMMP acts as a flame promoter (Reference 9). It is proposed that the DMMP catalyzes the recombination of •OH and •H free radicals.

Owing to the spectral richness associated with phosphorus in flames (e.g., Reference 10), a large amount of spectroscopic work has been accomplished on phosphorus in combustion processes. A quantitative study of the emission spectra of counterflow diffusion flames of ethylene, methane, or hydrogen burning with air has been made for addition of the inhibitors methyl bromide (CH_3Br), bromine (Br_2), carbon tetrachloride (CCl_4), chlorine (Cl_2), or phosphorus oxychloride ($O{=}PCl_3$) to either the air or fuel supply (Reference 11). Specific effects occur for various fuels and inhibitors, but in general, •OH and HCO• emission decreases, C_2 increases, and CH varies little with increasing inhibitor concentration. Of particular interest is that phosphorus oxychloride gives the greatest reduction in •OH and also gives the largest inhibiting action of the agents tested for methane and ethene fuels. It is proposed that the inhibitors remove •OH radicals and, secondarily, promote formation of carbon particulate, which increases radiation losses and cools the flame. It is proposed that the extinguishment action of $POCl_3$ is due to the chlorine and that its high efficiency is due to ready formation of HCl in the flame.

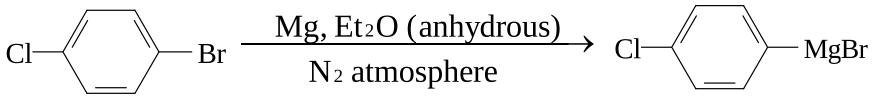
2. Flame Retardants

A search of the Chemical Abstracts Database for the key words “flame,” “fire,” and “flammable” coupled with “phosphonitriles” and related terms yielded 366 references, nearly all of which were for fire retardants for polymers. Recently identified reviews of cyclo- and polyphosphazenes as fire retardants and as fire resistant materials are contained in References 12 and 13.

A number of interesting and potentially important papers were presented at the Business Communications Company (BCC) Conference on Flame Retardancy, in Stamford, CT, 2-4 June 1997. Phosphorus compounds appear to act as flame retardants by both condensed-phase and gas-phase mechanisms, depending on the compound and polymer (Reference 14). The mechanisms, however, are still widely debated.

Phosphorus and bromine behave as synergistic flame retardants, and the greatest synergism appears to be when the two elements are combined in the same molecule

(References 15 and 16). It has been proposed that in polyesters, compounds containing both phosphorus and bromine act in two separate roles as flame retardants (Reference 17). The work cited indicates that the phosphorus induces formation of aromatic residues and char, which reduce the transport of gases to the flame. The bromine is believed to reduce the overall oxidation rate, reducing the heat transported back to the solid. The preparation of halogenated triaryl phosphines as flame retardants has been reported (Reference 18). An example is shown in Reactions 1 and 2 for tris(parachlorophenyl)phosphine (solid, melting point 106 °C). A number of phosphonium salts were prepared as shown in Reaction 3, where R_1, R_2, and R_3 are various alkyl and aryl groups. All of these materials are, of course, solids.



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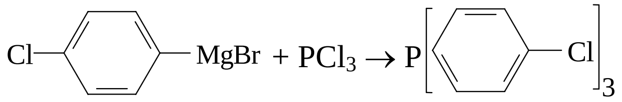

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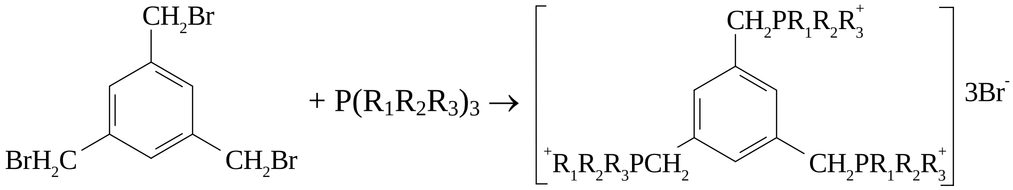

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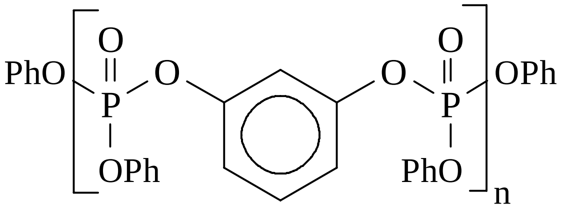
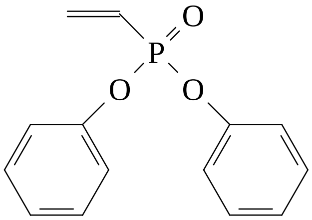
Resorcinol bis(diphenyl phosphate) (I, n = 1 to 8), a polymeric material containing no halogen, has been reported to act as a flame retardant additive (Reference 19). The material, which is made from phosphorus oxychloride, resorcinol, and phenol, is a colorless to light yellow liquid with a viscosity of 600 cp at room temperature and 100 cp at 55 °C.



(I)

Phosphorus-containing groups have been incorporated directly onto polymeric molecules rather than using phosphorus additives to provide flame retardancy. Fire resistant organosilicon polymers have been prepared by incorporation of phosphazenes (Reference 20). Resins containing melamine combined with triethyl phosphate and dimethyl methylphosphonate have been reported as flame retardants (Reference 21). A number of compounds containing vinyl groups attached to phosphorus have been prepared to permit copolymer formation (e.g., II and III, Reference 22). It is believed that when incorporated directly into a polymer, these materials provide flame retardancy primarily by char formation.



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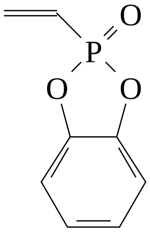


(III)

3. Flame Inhibition Mechanisms

Among the most important free-radical recombinations in both extinguishment by chemically active agents and combustion are combination of hydrogen atoms to form diatomic hydrogen and recombination of hydroxyl free radical with hydrogen atoms to form water. In the absence of catalysis, these reactions require the presence of a third body (M) to carry off excess energy (Reactions 4 and 5).

$$\bullet H + \bullet H + M \rightarrow H_2 + M^* \quad (4)$$

$$\bullet H + \bullet OH + M \rightarrow H_2O + M^* \quad (5)$$

Catalytic cycles have been proposed to accelerate Reactions 4 and 5 by phosphorus-containing compounds. Hastie and Bonnell (Reference 23) have proposed three cycles (Reactions 6 through 8; 9 and 10; and 11 and 12) for recombination of hydrogen atoms to form diatomic hydrogen.

$$\bullet H + \bullet PO_2 + M \rightarrow HOPO + M^* \quad (6)$$

$$\bullet H + HOPO \rightarrow \bullet PO + H_2O \quad (7)$$

$$H_2O + \bullet PO \rightarrow \bullet PO_2 + H_2 \quad (8)$$

$\bullet H + \bullet PO + M \rightarrow HPO + M^*$ (9)

$\bullet H + HPO \rightarrow \bullet PO + H_2$ (10)

$\bullet H + \bullet PO_2 + M \rightarrow HOPO + M^*$ (11)

$\bullet H + HOPO \rightarrow \bullet PO_2 + H_2$ (12)

Twarowski has observed large increases in the relaxation rate of •OH to equilibrium concentrations following H_2O photolysis (References 24 through 26). Mixtures of phosphine (PH_3), oxygen, hydrogen, and argon were ignited in a stirred-flow reactor, and the products were passed into a chamber where the H_2O product was photolyzed. From the data generated and reaction modeling with sensitivity analysis, three cycles were proposed as the predominant pathways for recombination of •H and •OH radicals to form H_2O. The first cycle involves three steps (Reactions 13 to 15), one of which (Reaction 14) involves no phosphorus containing species. $\bullet PO_2$ is consumed in a ternary reaction step (Reaction 13) and then regenerated (Reaction 15). In the second proposed reaction cycle, $\bullet PO_2$ is consumed in a ternary reaction step (Reaction 16). This is followed by a two-body reaction completing the •H + •OH recombination and regenerating $\bullet PO_2$ (Reaction 17). In the third cycle (Reactions 18 and 19), •PO is the catalytic species. Consideration of the sensitivity analysis results, species abundance, and rates indicates that the first catalytic cycle is the most important and that the third cycle is the least important. The ternary step in the second and third cycles involves reactions with •OH (Reactions 16 and 18), which are suggested to be slower than the ternary reaction with •H in Reaction 13. Moreover, the low abundance of •PO compared to $\bullet PO_2$, makes the third cycle even less favorable.

$\bullet H + \bullet PO_2 + M \rightarrow HOPO + M^*$ (13)

$\bullet OH + H_2 \rightarrow H_2O + \bullet H$ (14)

$\bullet H + HOPO \rightarrow H_2 + \bullet PO_2$ (15)

$\bullet OH + \bullet PO_2 + M \rightarrow HOPO_2 + M^*$ (16)

$\bullet H + HOPO_2 \rightarrow H_2O + \bullet PO_2$ (17)

$\bullet OH + \bullet PO + M \rightarrow HOPO + M^*$ (18)

$\bullet H + HOPO \rightarrow H_2O + \bullet PO$ (19)

An alternative cycle, in which Reactions 14 and 15 are replaced by Reaction 20 is possible; however, Reaction 20 does not appear to be as rapid as the first two under the experimental conditions used in the studies cited above (References 24 through 26).

$$HOPO + \bullet OH \rightarrow \bullet PO_2 + H_2O \tag{20}$$

Further calculations and modeling by Twarowski indicate that due to the highly coupled reaction system, the accelerated formation of H_2O from •H and •OH appears to be highly dependent on H_2 formation by the cycle of Reactions 11 and 12 (Reference 27).

Molecular beam mass spectrometry of the combustion of trimethylphosphate (TMP, $O{=}P(OCH_3)_3$) has indicated the processes shown in Reactions 21 and 22, both of which would allow elimination of hydrogen atoms (Reference 28).

$$O{=}P(OCH_3)_3 + \bullet H \rightarrow O{=}P(OH)(OCH_3)_2 + \bullet CH_3 \tag{21}$$

$$O{=}P(OCH_3)_3 + \bullet H \rightarrow O{=}PH(OCH_3)_2 + \bullet OCH_3 \tag{22}$$

B. CHEMISTRY

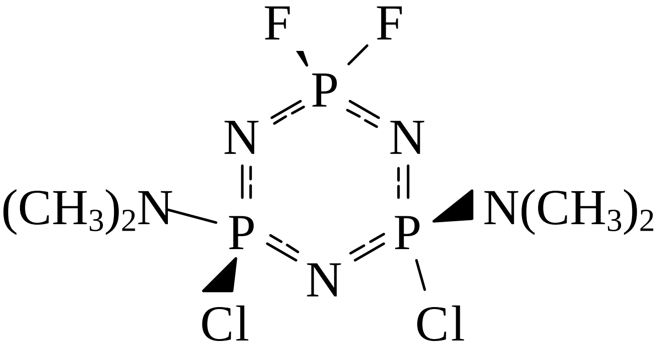
Phosphorus chemistry has been the subject of a number of relatively recent reviews (e.g., the papers in Reference 29); however, most of this work has been on nonvolatile or flammable chemicals. Again, Reference 3 provides a good overview of phosphorus chemistry as it applies to chemicals of interest as fire suppressants. Only updated information or newly identified references are presented here.

1. Phosphonitriles

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

The linear phosphonitriles, for which preparations have been reported (Reference 30), are considerably more reactive than the cyclic compounds, particularly toward hydrolysis (Reference 31). This makes them somewhat less attractive than the cyclic materials for study as halon replacements. The reactivity of the 3-membered ring system $P_3N_3Cl_6$ toward chloride exchange is lower than that of the four-membered and larger cyclics (Reference 32).

Of particular interest are the fluorinated phosphonitriles. Fluorination normally occurs as geminal substitution; however, procedures for making nongeminal derivatives have been reported (Reference 33). Although a number of chloro- and fluoro-substituted bis(dimethylamino)cyclotriphosphonitriles have been reported (Reference 34), most of these are solids. Compound IV is, however, a liquid.



(IV)

Bromine-containing phosphonitriles are of some interest due to the potential for fire extinguishment contribution by bromine and for possible synergism between bromine and phosphorus. The fully brominated compounds are solids or oils (Reference 35) and are, therefore, unlikely to be appropriate for investigation as fire extinguishants, though they may have other uses (e.g., flame retardants). Crown ether complexes have been used to prepare the highly colored solid compound NP_2Br_9 from KBr and hexachlorocyclotriphosphonitrile ($P_3N_3Cl_6$) (Reference 36). This compound can then be heated to form the more stable NP_2Br_7. Structures are given for neither of these materials. The preparation of mixed fluorine- and bromine-substituted phosphonitriles have been prepared by reaction of silver fluoride with $P_3N_3Br_6$ (Reference 37); however, the properties are not given.

Mixed methyl- and fluorine-substituted phosphonitriles have been prepared by reaction of octafluorocyclotetraphosphonitrile with methyl lithium (References 38 and 39). The compounds are high boiling liquids and solids. Derivatives with *tert*-butyl and *n*-butyl substituents (References 40 and 41) and with 1- and 2-propenyl substituents (Reference 42) have also been reported.

2. Fluoroalkyl Phosphines

In Reference 3, we noted that at high temperatures and pressures, phosphorus reacts with a number of fluoroalkyl iodides (RI) to give compounds having the structure PRI_2, PR_2I, and PR_3; however, we did not cite the references nor did we go into this any further other than to make a mixture of the iodo and diiodo compounds with fluoropropyl groups. The presence of fluorine in the alkyl groups of these materials greatly decreases their basicity (Reference 43) and could, by analogy with the amines, decrease toxicity. Owing to the simplicity of these materials and, in particular, the interest in the perfluorinated trialkylphosphines, these compounds were examined further under this project.

The simplest member of the perfluorinated trialkyl is tris(trifluoromethyl)-phosphine ($(CF_3)_3P$), which has been prepared as a mixture with trifluoromethyldiiodophosphine ($(CF_3)PI_2$) and bis(trifluoromethyl)iodophosphine ($(CF_3)_2PI$) by reaction of phosphorus with trifluoroiodomethane (CF_3I) (Reference 44) and also by reaction of tris(diethylamino)phosphine ($P(N(C_2H_5)_2)_3$) with trifluoromethyl bromide ($CBrF_3$, Halon 1301) and triphenylphosphite ($O{=}P(OC_6H_5)_3$) in tris(dimethylamino)phosphine oxide ($OP(N(CH_3)_2)_3$, hexamethylphosphoramide, HMPA) (Reference 45). Unfortunately this material (like some of its complexes, Reference 46) is spontaneously flammable (Table 2). The iodide derivatives are exceedingly useful precursors for a number of compounds of interest here; however, even with optimized procedures (Reference 47), the syntheses are difficult, and the reactants and products are hard to handle. Reaction of $(CF_3)_2PI$ with mercury gives the flammable compound tetrakis(trifluoromethyl)diphosphine ($(CF_3)_2PP(CF_3)_2$) (Reference 44) and the tetrameric and pentameric cyclic compounds $(CF_3P)_4$ and $(CF_3P)_5$ (Reference 48) (Table 2). The compounds $(CF_3)PF_2$ and $(CF_3)_2PF$ are also known (Reference 49).

TABLE 2. FLUOROALKYL PHOSPHINES.

Compound	Boiling point, °C	Properties	Reference
$(CF_3)_3P$	17	Spontaneously flammable	44
$(CF_3P)_4$	Not available	Solid, melting point 66.4 °C	48
$(CF_3P)_5$	190	Not available	48
$(CF_3)_2PP(CF_3)_2$	83-84	Flammable	44
$(C_2F_5)_3P$	70	Not available	43

The higher molecular weight perfluoroalkyl derivatives are likely to be more stable than the methyl compounds. Tris(pentafluoroethyl)phosphine ($(C_2F_5)_3P$), a liquid boiling at 70 °C, has been prepared by reaction of phosphorus trichloride (PCl_3) with ethyl lithium (C_2F_5Li), which can be prepared by reaction of chloropentafluoroethane (C_2F_5Cl) with n-butyl lithium (C_4F_9Li) (Reference 43). The procedure, however, has not been published. It has proven impossible to prepare the tris(heptafluoropropyl)phosphine ($(C_3F_7)_3P$), apparently due to steric hindrance (Reference 50).

A large number of trifluoromethyl-substituted diphosphorus compounds having the general formula $(CF_3)_2PRP(CF_3)_2$, where “R” represents a branched or linear hydrocarbon or fluorocarbon chain, have been synthesized as bidentate ligands starting with $(CF_3)_2PP(CF_3)_2$ (Reference 51 and 52). It has been stated that these compounds are difficult to prepare owing to difficulty in synthesis of the diphosphine precursor (Reference 43). These materials, though liquid, have relatively high boiling points. A similar compound has also been prepared: $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$, boiling point 105 °C at 80 torr (Reference 53). The primary interest in these compounds is as bidentate ligands (Reference 54).

3. Amino Fluoroalkylphosphines

Aminobis(trifluoromethyl)phosphines ($(CF_3)_2PNR_2$, R= $-H$, $-CH_3$) have been prepared by reaction of chlorobis(trifluoromethyl)phosphine ($(CF_3)_2PCl$) with the appropriate amine (Reference 55). Though these materials are relatively stable liquids (Table 3), they are readily oxidized in air (and the simplest amino compound is spontaneously flammable).

Moreover, the $(CF_3)_2PCl$ starting material is spontaneously flammable. Amines containing two and three bis(trifluorophosphine) groups (Reference 56) and compounds of the type $[(CF_3)_2N]_nP(CF_3)_{3-n}$, n=1-3 (the latter discussed further in Reference 3) have also been prepared (Table 3). The starting materials, however, are also spontaneously flammable—$(CF_3)_2PCl$ or tris(trifluoromethyl)phosphine ($(CF_3)_3P$). Aminobis(heptafluoropropyl)phosphine ($(C_3F_7)_2PNH_2$), a high boiling liquid (Table 3), has been prepared by reaction of $(C_3F_7)_2PCl$ with anhydrous ammonia (Reference 50). As is typical for all of these reactions, the starting material was prepared by reaction of heptafluoropropyl iodide with phosphorus at high temperature and pressure followed by replacement of the iodide with chloride using silver chloride.

TABLE 3. AMINO FLUOROALKYLPHOSPHINES.

Compound	Boiling point, °C[a]	Properties	Reference
$(CF_3)_2PNH_2$	67.1	Spontaneously flammable	55
$(CF_3)_2PNH(CH_3)$	72.3	Not available	55
$(CF_3)_2PN(CH_3)_2$	83.2	Not available	55
$((CF_3)_2P)_2NH$	Not available	Vapor pressure 46.7 torr at 23.9 °C	56
$((CF_3)_2P)_2NCH_3$	Not available	Vapor pressure 17.3 torr at 25.0 °C	56
$((CF_3)_2P)_3N$	Not available	Solid, melting point 36.5-36.8 °C	56
$(CF_3)_2NP(CF_3)_2$	51	Stable at room temperature	57
$((CF_3)_2N)_2P(CF_3)$	92.5	Stable at room temperature	57
$((CF_3)_2N)_3P$	135	Stable at room temperature	57
$(C_2F_7)_2PNH_2$	143	Not available	50

[a] One atmosphere (nominal) pressure.

4. Phosphorus(III) Acids and Esters

The phosphorus(III) acids of interest are the trioxy acid, which can be formulated as the hypothetical phosphorous acid ($P(OH)_3$) but actually exists as phosphonic ("ortho-phosphorous") acid ($O{=}PH(OH)_2$); the dioxy acid phosphinic ("hypophosphorous") acid ($O{=}PH_2(OH)$); and the monooxy phosphinous acid ($O{=}PH_3$). A major problem exists when discussing the esters of these acids, since more than one form is often possible, and the actual structure may be unknown (Reference 3). The tri-, di-, and mono-esters of phosphorous acid are the phosphites $P(OR)_3$, $P(OH)(OR)_2$,and $P(OH)_2(OR)$, which often rearrange to the phosphonate structures, of which there are five possibilities: $O{=}PR(OR)_2$, $O{=}PH(OR)_2$, $O{=}PR(OH)(OR)$, $O{=}PH(OH)(OR)$, and $O{=}PR(OH)_2$. These latter five structures are formally derivatives of phosphonic acid. The esters of phosphinic acid (the phosphinites) are $O{=}PH_2(OR)$, $O{=}PHR(OR)$, and $O{=}PR_2(OR)$. Phosphites ($P(OR)_3$) are rather easily prepared by reaction of PCl_3 in anhydrous ether with an alcohol in the presence of the base pyridine (Equation 23). Appropriate conditions will also give the phosphonates $O{=}PH(OR)_2$ and $O{=}PH_2(OR)$ or the phosphites $P(OH)_2(OR)$ and $P(OH)(OR)_2$.

$$PCl_3 + 3ROH \rightarrow P(OR)_3 + 3HCl \tag{23}$$

Tris(hexafluoroisopropyl)phosphite ($P(OCH(CF_3)_2)_3$) has been prepared and used as a ligand in a metal catalyst (Reference 58). The phosphinous acid $(CF_3)_2POH$ has been prepared in a rather complex series of steps with $(CF_3)_2POP(CF_3)_2$ as the immediate precursor (Reference 59). Esters are known, and, unlike the nonfluorinated compounds, are stable toward $PR_2(OR) \rightarrow O{=}PR_3$ rearrangement (Reference 60). The heptafluoropropyl phosphonous acid ($(C_3F_7)P(OH)_2$ or $O{=}PH(C_3F_7)(OH)$) has been reported (Reference 50). Routes to other perfluoroalkylphosphonic and perfluoroalkylphosphinic acids ($O{=}PR_2(OH)$ and $O{=}PR(OH)_2$, $R = -CF_3, -C_2F_5, -n\text{-}C_3F_7, -n\text{-}C_4F_9$) have been described (References 50 and 61). Like many of the fluoroalkyl phosphorus compounds involving direct carbon-phosphorus bonds, the first steps involve the difficult syntheses of R_2PI and RPI_2. Syntheses of a number of fluoroalkyl acid phosphates and precursor phosphorus compounds have also been reported (Reference 62).

5. Phosphorus(V) Acids and Esters

The parent acid is orthophosphoric acid ($O{=}P(OH)_3$), with condensed structures containing one or more P-O-P groups known. The esters of phosphoric acid are the triester $O{=}P(OR)_3$ and the acid phosphates $O{=}P(OH)_2(OR)$, and $O{=}P(OH)(OR)_2$. With four oxygen atoms, the multiple structures found for the phosphorus(III) esters do not occur.

6. Phosphoranes

A number of fluorophosphoranes (pentacoordinate phosphorus(V) compounds), including some amino-substituted products have been described (References 63 and 64).

Although all of these contain phosphorus-fluorine bonds (making them unlikely candidates as halon replacements), the boiling points are in acceptable ranges for a number of compounds. Unfortunately, none of the alkyl derivatives in the sources cited is fluorinated.

C. ACQUISITION AND TESTING

Consideration of the information presented above indicated that phosphonitriles were not ideal for testing owing to their low volatility and that phosphines were likely to be too toxic to consider, except possibly for mechanistic studies. Table 4 presents phosphorus-containing compounds selected for testing.

1. Tris(2,2,2-trifluoroethyl)phosphate

Synthesis of tris(2,2,2-trifluoroethyl)phosphate ($O{=}P(OCH_2CF_3)_3$) was attempted by reaction of phosphorus(V) oxychloride ($O{=}PCl_3$) with 2,2,2-trifluoroethanol (CF_3CH_2OH) in pyridine (Reaction 24). This synthesis is similar to that used to prepare the monoester, (2,2,2-trifluoroethyl)phosphate ($O{=}P(OCH_2CF_3)_3$) (Reference 65).

$$O{=}PCl_3 + 3CF_3CH_2OH \xrightarrow{\text{pyridine}} O{=}P(OCH_2CF_3)_3 + 3HCl \qquad (24)$$

The pyridine acts as an hydrogen acceptor giving the insoluble hydrochloride salt as a byproduct. Pyridine (0.42 mL, 0.0052 mole) and 2,2,2-trifluoroethanol (0.52 mL, 0.0072

TABLE 4. PHOSPHORUS-CONTAINING COMPOUNDS SELECTED FOR TESTING.

Compound	Formula	Boiling point, °C (torr)	Flash point, °C
Tris(2,2,2-trifluoroethyl)phosphate	$O{=}P(OCH_2CF_3)_3$	Not available	Not available
Dimethylmethylphosphonate	$O{=}P(CH_3)(OCH_3)_2$	[a]181	[a]68
Trimethylphosphate	$O{=}P(OCH_3)_3$	197	None
Trimethylphosphite	$P(OCH_3)_3$	111-112	27
(Bromodifluoromethyl) diethylphosphonate	$O{=}P(CBrF_2)(C_2H_5)_2$	[b]99-102 (16) [c]220 (760)	Not available
Hexamethylphosphoramide	$O{=}P[N(CH_3)_2]_3$	230-232 (740)	Not available
Bis(2,2,2-trifluoroethyl)phosphite	$O{=}PH(OCH_2CF_3)_2$	[a]43-44 (2) [c]190 (760)	[a]76
Tris(2,2,2-trifluoroethyl)phosphite	$P(OCH_2CF_3)_3$	[a]130-131 (743)	[a]>110

[a]Reference 66.
[b]Reference 67.
[c]Estimated using pressure-temperature nomograph.

mole) were introduced by syringe into a 250-mL round-bottom flask and mixed by gentle swirling of the stoppered flask. To this mixture, 0.1 mL (0.0011 mole) of phosphorus(V) oxychloride was added by syringe. Instantaneous fuming and a slight warming of the flask was observed with an almost immediate precipitation of clear crystalline material. The flask and its liquid contents were swirled frequently to ensure mixing and reaction, and the mixture was allowed to sit for 48 hours. Direct injection gas chromatography (GC) employing a 30M capillary column and isothermal (34 °C) conditions of the reaction product showed two major peaks with retention times of 5.49 and 12.02 min. A minor peak representing only 3 percent of the total combined integrated GC peak areas was observed at 1.10 min.

GC/MS analysis showed four peaks eluting at retention times (RT) of 1.34 min (2.9 percent), 1.48 min (12.6 percent), 3.99 min (58.9 percent), and 7.52 min (25.5 percent), where values in parentheses are the percentages of the total peak areas. Software-based peak identifications were performed for each GC peak employing a cut off of 90 percent for acceptance of the quality of fit of observed ion abundance peak pattern comparisons to library data. The software-based assignments were RT 1.34, unknown; RT 1.48, 2,2,2-trifluoroethanol; RT 3.99, pyridine; and RT 7.52, unknown. The RT 7.52 peak had major ion peaks at 324, 325, and 275 amu consistent with the loss of HF, F and CF_3, respectively from $O{=}P(OCH_2CF_3)_3$. The mass peak at 245 amu could result from additional loss of H_2CO (formaldehyde) from the 275-amu ion or loss of OCH_2CF_3 ion from the parent molecule (more likely). Although no parent mass peak (344 amu) was observed, it is likely that the RT 7.52 GC peak was $O{=}P(OCH_2CF_3)_3$.

Insufficient product was obtained during this synthesis to perform cup-burner testing. However, it is planned that larger scale syntheses will be carried out in the future. Commercial sources were used for the remaining compounds in this section.

2. Dimethylmethylphosphonate

Testing of dimethylmethylphosphonate ($O{=}P(CH_3)(OCH_3)_2$) was attempted using the Standard NMERI Cup Burner. Due to its low volatility (boiling point 181 °C), the material was difficult to volatilize without excessive heating in the heated cup-burner mixing chamber. This excessive heat apparently caused some decomposition since a black, tarry substance was obtained. A single test that appeared to have the least difficulties gave an extinguishing concentration of 5 vol.%. Since some condensation on the glass beads above the mixing chamber and decomposition may have occurred, this value should be considered a maximum because not all of the compound was available to extinguish the fire.

3. Trimethylphosphate

Trimethylphosphate ($O{=}P(OCH_3)_3$) was tested using the Modified NMERI Cup Burner. Due to its high boiling point (197 °C), this compound was extremely difficult to test. The first run gave an extinguishment concentration of 6.60 vol.%; however, this value may be slightly high since it was observed that a small amount of the compound did not volatilize in the mixing chamber (which was maintained at 145 °C) at the point of extinguishment. With a higher mixing chamber temperature (328 °C), an extinguishment concentration of 6.85 vol.% was obtained. Again, some of the compound in the mixing chamber did not volatilize. At an even higher mixing chamber temperature (344 °C), a lower cup-burner value of 5.3 vol.% was obtained; however, this value is suspect since the chimney temperature was sufficiently high (156 °C) that the *n*-heptane in the fuel cup boiled and was difficult to control.

4. Trimethylphosphite

Trimethylphosphite ($O{=}P(OCH_3)_3$), with a boiling point of 111-112 °C, provided few operational problems with the Modified NMERI Cup Burner. The compound was, however, sufficiently flammable that it ignited at the glass beads. Moreover, complete extinguishment of the *n*-heptane flame was not achieved. Cup-burner testing of this compound was, therefore, suspended. In separate testing, the compound ignited with difficulty with a butane ignitor and continued to burn once the flame was removed.

5. (Bromodifluoromethyl)diethylphosphonate

(Bromodifluoromethyl)diethylphosphonate ($O{=}P(CBrF_2)(C_2H_5)_2$) was tested using the Modified NMERI Cup Burner. Since only a small amount of material was available, the first test was used to determine an upper bound for the extinguishing concentration with as little compound as possible. From the results (i.e., ready extinguishment, difficult/near extinguishment, no extinguishment) of a fixed and relatively high flow rate, it was hoped to estimate the flow rate for subsequent tests. During the first test, the flame extinguished readily at a concentration of 4.73 vol.%. The second test employed a much lower flow rate (approximately one-third that of the first test). Even though the temperature of the heated chamber at the base of the cup burner was 250 °C, it appeared that the compound did not volatilize completely. The flame continued to show some extinguishment from the compound after the syringe pump was turned off, which indicates that the compound in the mixing chamber continued to volatilize even after the agent supply was stopped. The temperature of the heated chamber was therefore increased to 300 °C.

During the next test, the compound appeared to volatilize well, and the flame was close to extinguishment; however, the *n*-heptane became sufficiently hot that boiling was observed. At this point, the agent concentration was 1.43 vol.%. Thus, the extinguishment concentration was estimated to be between 1.43 and 4.73 vol.%. A test with an increased flow rate and a slightly lower chamber temperature (270 °C) resulted in an extinguishment concentration of 3.29 vol.%. Although some condensation on the glass beads was observed, it was not considered significant. Thus, the cup-burner extinguishment concentration is higher than 1.43 vol.% (since extinguishment did not occur at that concentration although there was good volatilization) and lower than 3.29 vol% (since extinguishment was obtained at that concentra-tion without complete volatilization).

6. Hexamethylphosphoramide

Testing of hexamethylphosphoramide ($O{=}P[N(CH_3)_2]_3$) was extremely difficult due to its high boiling point and low vapor pressure. Using the highest possible heating chamber temperatures, a maximum concentration of 8.70 vol.% could be obtained, which neither extinguished the flame nor reduced its size.

7. Bis(2,2,2-trifluoroethyl)phosphite

Bis(2,2,2-trifluoroethyl)phosphite was tested using the Modified NMERI Cup Burner. Inadequate vaporization was observed even for heating chamber temperatures of 200 °C. The compound continued to boil in the bottom of the mixing chamber for 3.5 min after the syringe pump was turned off. Moreover, condensation on the glass beads above the mixing chamber was obvious. This is not surprising since the boiling point of this compound is 43 °C at 2 torr (estimated to be 190 °C at 760 torr by a pressure/temperature nomograph). Thus, testing was discontinued.

8. Tris(2,2,2-trifluoroethyl)phosphite

Tris(2,2,2-trifluoroethyl)phosphite was tested using the Modified NMERI Cup Burner, house air, and a heating chamber temperature of 120 °C. Tests were reproducible, with extinguishment concentrations of 2.18, 2.61, and 2.59 vol.% (average 2.43 ± 0.17 vol.%).

In a second series, tests were run using the Standard NMERI Cup Burner apparatus and bottled breathing air (medical quality) with a heating chamber temperature of 200 °C. Extinguishing concentrations of 1.22, 1.27, 1.43, 1.47, 1.57, 1.52, 1.57, 1.33, 1.33, and 1.47 vol.% (average 1.41 ± 0.11 vol.%) were obtained.

The very large difference may have been due to inadequate volatilization in the heated mixing chamber in the first series; however, in that series, the compound appeared to vaporize completely in the mixing chamber without condensation on the beads in the cup burner. It also may have resulted from the use of different air sources. To check the latter, the *n*-heptane extinguishment concentration of HFC-125 (CHF_2CH_3) was determined with the Standard

NMERI Cup Burner using both bottled breathing air and house air. The measured concentrations were 7.44, 7.49, 7.74, 7.85, and 7.81 vol.% (average 7.66 ± 0.16 vol.%) with the bottled air and 8.43, 8.52, 8.33, 8.38, and 8.38 vol.% (average 8.41 ± 0.06 vol.%) with the house air. Further investigation indicates that the oxygen content of the bottled air was low. Only the results of the house air determination are therefore used in this report.

SECTION III

SILICON

A review of the chemistry and fire suppression properties of silicon compounds has been presented in Reference 68. Except as otherwise stated, all of the information presented here is newly acquired or is an expansion of information contained in that source. Of particular interest as fires suppressants are silicon-containing compounds with fluorinated alkyl groups. Fluoro-organosilicon polymers have been of some commercial interest (Reference 69).

A. FIRE SUPPRESSION

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

Overall, there is little evidence that silicon, itself, plays a significant role in flame extinguishment, even though one could propose combustion free radical recombination cycles such as those in Reactions 25 and 26, similar to those proposed for other metals (Reference 5). It is difficult to determine why such cycles are favorable in some cases and not in others.

$$\mathrm{SiO\bullet + \bullet H + X \rightarrow SiOH + X^*} \qquad (25)$$

$$\mathrm{SiOH + \bullet H \rightarrow H_2 + SiO\bullet} \qquad (26)$$

The combustion and explosive properties of dichlorosilane (SiH_2Cl_2) have been thoroughly studied (Reference 70). Polyorganosiloxanes and inorganic silicates have been examined as potential flame retardants (Reference 71). The major mode of reaction is apparently formation of protective surface coatings during a fire. The flammability of silicone polymers has been reduced through addition of fluorine, bromine, and CCl_3 groups (Reference 72).

Claims have been made that liquid fire extinguishing compositions containing haloalkanes and cyclic polysiloxanes increase penetration and throw distance (Reference 73); however, there is no claim that the silicon-containing compounds actually increase the intrinsic fire suppression capability.

B. CHEMISTRY

Silicon chemistry has been the subject of a number of relatively recent reviews (e.g., the papers in Reference 74); however, the number of nonflammable silicon compounds that can be considered for use in this project is small.

1. Bromoalkylsilanes

A series of bromoalkylsilanes has been prepared in a two-step synthesis from a halomethane and a bis(trimethylsilyl)amide (Reference 75). The preparation is shown in Reactions 27 and 28, where “M” is sodium or potassium and “R” is a nonfluorinated (compounds containing fluorine on a carbon atom adjacent to silicon are usually unstable) haloalkyl group.

$$(M^+ [(CH_3)_3Si]_2N^-) + RH \rightarrow [(CH_3)_3Si]_2NH + (M^+ R^-) \tag{27}$$

$$(M^+ R^-) + (CH_3)_3SiCl \rightarrow (CH_3)_3SiR + MCl \tag{28}$$

The reaction of trialkylchlorosilane ($SiClR_3$) with chlorotrifluoroethene ($CClF{=}CF_2$) allows the synthesis of a number of trifluorovinylsilanes ($CF_2{=}CFSiR_3$) (Reference 76). Bromination or hydrobromination of the double bond may permit the formation of the compounds $CBrF_2CBrFSiR_3$, $CBrF_2CHFSiR_3$, and $CHF_2CBrFSiR_3$.

2. Fluoroalkoxysilanes

A series of tetrafluoroalkoxysilanes (Si(OR)4) has been prepared by reaction of the appropriate fluorinated alcohol with silicon tetrafluoride (SiF_4) (Reference 77). All of the

TABLE 5. TETRA(FLUOROALKOXY)SILANES.

Name	Formula	Boiling point, °C (torr)	Liquid density g/mL (°C)	Liquid viscosity, 20°C, cp
tetrakis(2,2,2-trifluoroethoxy)silane	$Si(OCH_2CF_3)_4$	155.5 - 157 (743)	1.5107 (20)	2.2089
tetrakis(2,2,3,3-tetrafluoropropoxy)silane	$Si(OCH_2CF_2CHF_2)_4$	117 - 118 (4)	1.5927 (20)	18.92
tetrakis(2,2,3,3,4,4,4-heptafluorobutoxy)silane	$Si(OCH_2(CF_2)_2CF_3)_4$	96 - 97 (4)	1.5740 (71.1)	7.613
tetrakis(2,2,3,3,4,4,5,5-octafluoropentoxy)silane	$Si(OCH_2(CF_2)_3CHF_2)_4$	156 - 159 (2.5)	1.8150 (20)	42.75
tetrakis(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoropentoxy)silane	$Si(OCH_2(CF_2)_5CHF_2)_4$	201 - 204 (3)	1.7181 (71.1)	108.8
tetrakis(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluorononoxy)silane	$Si(OCH_2(CF_2)_7CHF_2)_4$	[a]235 - 240 (2.5)	Not reported	Not reported

[a]With decomposition.

compounds are liquids at room temperature with very low melting points (less than -68 °C except for $Si(OCH_2CF_3)_4$); however, the boiling points and viscosities are high (Table 5). One major problem with such alkoxy compounds is that they hydrolyze readily and then polymerize.

C. ACQUISITION AND TESTING

Due to the complexity of the syntheses, no attempt was made to prepare fluoroalkyl-containing silicon compounds during the present project. Table 6 contains those silicon compounds selected for testing to obtain at least some baseline data.

1. Silicon Tetrachloride

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

TABLE 6. SILICON-CONTAINING COMPOUNDS SELECTED FOR TESTING.

Compound	Formula	Boiling point, °C (torr)	Flash point, °C	Reference
Silicon tetrachloride	$SiCl_4$	57.6	None	66
Bromotrimethylsilane	$SiBr(CH_3)_3$	79	32	66
Silicon tetrabromide	$SiBr_4$	153	None	66

was attempted; however, with care, it is likely that the Modified NMERI Cup Burner could be used for this or similar compounds in the future.

2. Bromotrimethylsilane

Bromotrimethylsilane ($SiBr(CH_3)_3$) was tested using the Modified NMERI Cup Burner. With a boiling point of 79 °C, this compound is relatively easily volatilized; however, the material is flammable. Two tests gave cup-burner extinguishment concentrations of 2.28 vol.%. As the flow rate of the compound was increased, there appeared to be some effect on the flame, although no distinct lifting of the flame off of the fuel cup was observed. The flame wandered around, occasionally falling down the side of the cup. When the flow rate reached 0.043 g/s, the flame behaved erratically and traveled to the bottom of the chimney (to the glass beads). The flame in the fuel cup was extinguished, but the compound continued to burn on the surface of the glass beads. A small amount of the compound was found to sustain a flame.

3. Silicon Tetrabromide

As expected, silicon tetrabromide ($SiBr_4$) was more effective than the other silicon compounds tested. The first test with the Modified NMERI Cup Burner gave an extinguishment concentration of 2.04 vol.%. During subsequent testing, however, serious problems with clogging of the syringe pump were encountered. Cleaning the syringe completely and repeating the test resulted in the same problem. This problem casts doubt on the extinguishment value of 2.04 vol.% obtained in the first test. If the syringe was sticking, the measured flow rate would be less than the actual flow rate, because the syringe pump is allowed to slip for safety. This would result in a low cup-burner value.

SECTION IV

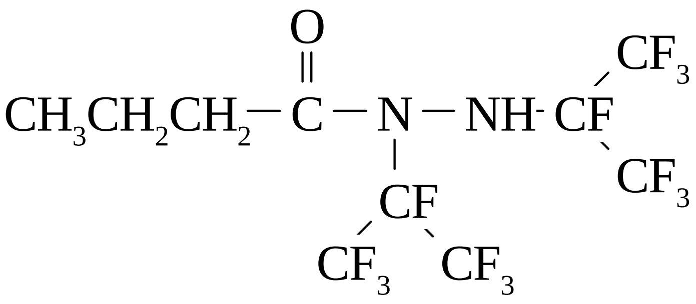
AMINES

A relatively short discussion of the chemistry and fire suppression properties of amine compounds has been presented in Reference 78. Except as otherwise stated, all information presented here is newly acquired or is an expansion of information contained in that source.

A. FIRE SUPPRESSION

Fluorinated derivatives of carboxylic acid hydrazides having the general formula $RC(O)N(CF_2X)NHCF_2X$, where R is a hydrocarbon and X is fluorine, perfluoroalkyl, or ω-hydroperfluoroalkyl, are reported to be nonflammable and, in some cases, to act as fire extinguishants (Reference 79). The compounds can be prepared by reaction of an aldehyde with a polyfluoroazoalkane (Reaction 29). One example of a fire extinguishing compound of this type is N,N'-bis(perfluoropropyl)-N-butyrohydrazide (V).

$$RC(O)H + CF_2XN{=}NCF_2X \rightarrow RC(O)N(CF_2X)NHCF_2X \qquad (29)$$



(V)

B. CHEMISTRY

Appendix A contains a list of all fluorinated amines contained in the CGET Chemical Options Database (CCOD) with the ID number for each. The following chemical information is additional to that found in Reference 78.

N-Bromobistrifluoromethylamine ($(CF_3)_2NBr$) adds to the unsaturated compounds tetrafluoroethene ($CF_2=CF_2$), trifluoroethene ($CHF=CF_2$), 1,1-difluoroethene ($CH_2=CF_2$), *cis*-1,2-difluoroethene ($CHF=CHF$), ethene ($CH_2=CH_2$), hexafluoropropene ($CF_2=CFCF_3$), chlorotrifluoroethene ($CClF=CF_2$), and 1,2-dichlorodifluoroethene ($CClF=CClF$) under mild conditions, to give the 1:1 adducts in high yield. The $(CF_3)_2N$ attaches only to the CH_2 group of 1,1-difluoroethene, whereas trifluoroethene gives the isomers $(CF_3)_2NCHFCF_2Br$ (78%) and $(CF_3)_2NCF_2CHFBr$ (22%). Hexafluorocyclobutene and octafluorobut-2-ene require more drastic conditions, and give the olefin dibromide and tetrakistrifluoromethylhydrazine rather than addition of the N-bromo-compound (Reference 80). The properties of the compounds of interest are shown in Table 7.

TABLE 7. BROMOALKYLAMINES.

Compound	Boiling point, 1 atmosphere, °C
$(CF_3)_2NCH_2CH_2Br$	[a]85.6
$(CF_3)_2NCH_2CBrF_2$	79.9
$(CF_3)_2NCHFCHBrF$	76.4
$(CF_3)_2NCHFCBrF_2$	62.4
$(CF_3)_2NCF_2CHBrF$	74.0
$(CF_3)_2NCF_2CBrF_2$	60.9
$(CF_3)_2NCF_2CBrClF$	93.5
$(CF_3)_2NCFClCBrClF$	125.6
$(CF_3)_2NCF_2CBrFCF_3$	82.2

[a] Also reported as 141 °C (Reference 81).

Reaction of N-bromobistrifluoromethylamine ($(CF_3)_2NBr$) with ethyne ($CH\equiv CH$) gives $(CF_3)_2NCH=CHBr$, which a boiling point of 68.8 °C (Reference 81). This compound is of high interest in this project since the atmospheric lifetime should be quite short.

C. ACQUISITION AND TESTING

1. Chemicals for Testing

Table 8 is a list of nitrogen-containing compounds selected for testing.

TABLE 8. NITROGEN-CONTAINING COMPOUNDS SELECTED FOR TESTING.

Compound	Formula	Boiling point,°C	Reference
N,N-bis(trifluoromethyl) pentafluoroethanamine	$N(CF_3)_2(C_2F_5)$	[a]20 to 22	82
N,N-bis(trifluoromethyl) trifluoromethanamine	$N(CF_3)_3$	[a]-10	82

2. N,N-bis(trifluoromethyl)pentafluoroethanamine

N,N-bis(trifluoromethyl)pentafluoroethanamine ((pentafluoroethyl)bis(dimethyl)-amine, $N(CF_3)_2(C_2F_5)$) was obtained from Dr. Takashi Abe, National Industrial Research Institute (NIRI), Japan. Three tests were run with the Standard NMERI Cup Burner with house air and a gas delivery (measured with a bubble meter) to give extinguishment concentrations of 3.7, 3.8, and 3.8 vol.% (average 3.77±0.04 vol.%).

3. N,N-bis(trifluoromethyl)trifluoromethanamine

Synthesis of N,N-bis(trifluoromethyl)trifluoromethanamine (tris(trifluoromethyl)amine, $N(CF_3)_3$) was attempted using the procedure shown in Reaction 30. The two gases were mixed in a round bottom flask under room-temperature conditions, with both photolysis (UV) and heating. In all cases, the combination of the two gases resulted in formation of condensation on the flask walls. With photolysis, free iodine appeared to be generated as the vessel developed a light purple color. GC analysis indicated the formation of new peaks; all GC peaks eluted very early. No further work was done to prepare this material.

$$NH_3 + 3CF_3I \rightarrow N(CF_3)_3 + 3HI \tag{30}$$

SECTION V

FLUORINATED ETHERS

A. FIRE SUPPRESSION

Hydrofluoropolyethers (HFPE) are being introduced into the market, and there is some evidence for relatively good fire suppression performance (Reference 83). There is, however, little evidence that ethers provide any special mode of action in fire suppression.

B. CHEMISTRY

A list of fluorinated ethers contained in the CGET Chemical Options Database with the ID numbers and boiling points is contained in Appendix B.

C. ACQUISITION AND TESTING

1. Chemicals for Testing

Table 8 is a list of fluorinated ethers selected for testing.

TABLE 9. FLUORINATED ETHERS SELECTED FOR TESTING.

Compound	Formula	Boiling point, °C
1-methoxynonafluorobutane (Halocarbon No. HFE-E449s1)	$CF_3CF_2CF_2CF_2$-O-CH_3	[a]60
hydrofluoropolyether	$HF_2CO(CF_2O)n$- $(CF_2CF2O)_mCF_2H$	[b]100

[a] Grenfell, M. W., Klink, F. W., Owens, J. G., and Yanome, H., “New Fluorinated Solvent Alternatives,” Precision Cleaning '95, Rosemont, IL, 15-17 May 1995.

[b] Reference 84.

2. 1-Methoxynonafluorobutane

1-Methoxynonafluorobutane was obtained from 3M Company. Standard NMERI cup-burner testing gave an extinguishment concentration of 6.1 vol.%.

3. Hydrofluoropolyether

A mixture of hydrofluoropolyethers was obtained as an experimental product from Ausimont S.p.A. in Milano, Italy. Testing with the Standard NMERI Cup Burner gave an average extinguishment concentration of 5.1 vol.%.

SECTION VI
RESULTS AND CONCLUSIONS

A. MODIFIED NMERI CUP BURNER

During this project, the NMERI Cup Burner (Reference 2) was modified to use volume delivered by a syringe pump rather than weight to measure agent delivery rates. The use of a syringe pump has been demonstrated to allow cup-burner testing of high boiling point and/or viscous materials, particularly those that are difficult to pass through valves and delivery lines. Because the syringe pump delivery method allows less holdup of agent in lines and requires less storage, this method allows testing of agents available only in limited amounts. Overall, however, the use of weight is still the most accurate and reliable method for testing.

B. CUP-BURNER RESULTS

Table 10 gives the results of the cup burner testing. In a number of cases, the volatility (or flammability) was too high to give reliable results.

C. CONCLUSIONS

Of the families examined, phosphorus compounds provide the most promising candidates for continued work. Phosphines provide good materials for mechanistic studies; however, phosphines can be ruled out as candidates owing to their inherent low stability (many are flammable, sometimes spontaneously, even with fluorinated substituents) and high toxicities. Though it is possible to obtain fire extinguishment (sometimes, very good) with phosphazenes, these compounds have an inherently high molecular weight and, therefore, very low volatility. Of the phosphorus compounds, the esters of phosphorus-containing acids are the most promising candidates.

TABLE 10. CUP-BURNER TEST RESULTS.

Compound	Formula	Ext. conc., vol%	Comments
Tris(2,2,2-trifluoroethyl)phosphate	$O=P(OCH_2CF_3)_3$	---	synthesis incomplete
Dimethylmethylphosphonate	$O=P(CH_3)(OCH_3)_2$	5	single value with decomposition
Trimethylphosphate	$O=P(OCH_3)_3$	5.3-6.8	suspect value
Trimethylphosphite	$P(OCH_3)_3$	---	flammability prevented testing
(Bromodifluoromethyl) diethylphosphonate	$O=P(CBrF_2)(C_2H_5)_2$	<3.3	upper limit
Hexamethylphosphoramide	$O=P[N(CH_3)_2]_3$	>8.7	no extinguishment
Bis(2,2,2-trifluoroethyl)phosphite	$O=PH(OCH_2CF_3)_2$	---	volatility too low for test
Tris(2,2,2-trifluoroethyl)phosphite	$P(OCH_2CF_3)_3$	2.43	---
Silicon tetrachloride	$SiCl_4$	---	reaction with apparatus prevented testing
Bromotrimethylsilane	$SiBr(CH_3)_3$	2.28	---
Silicon tetrabromide	$SiBr_4$	2.04	suspect value
N,N-bis(trifluoromethyl)-pentafluoroethanamine	$N(CF_3)_2(C_2F_5)$	3.77	---
N,N-bis(trifluoromethyl)-trifluoromethanamine	$N(CF_3)_3$	---	synthesis incomplete
1-Methoxynonafluorobutane	$CF_3CF_2CF_2CF_2\text{-}O\text{-}CH_3$	6.1	---
Hydrofluoropolyether	$HF_2CO(CF_2O)n\text{-}(CF_2CF_2O)mCF_2H$	5.1	---

The primary problems of phosphorus-containing esters is their often high boiling points and viscosities and the flammability of many of the materials. Fluorination would, of course, aid in all of these problems. Thus, tris(2,2,2-trifluoroethyl)phosphite ($P(OCH_2CF_3)_3$) provides very good extinguishment. All other things being equal, compounds with phosphite structures are preferred over phosphonates or phosphates to increase the volatility. For example, bis(2,2,2-trifluoroethyl)phosphite ($O{=}PH(OCH_2CF_3)_2$), which actually has a phosphonate structure, has too low a volatility for a standard cup-burner test. Nevertheless, phosphates and phosphonates should not be dismissed. The most promising compounds would, therefore, be phosphites with formulas such as $P(OR_f)_3$, where R_f is a fluorinated group, which should have as low a molecular weight and as high a fluorination as possible. First, tris(2,2,2-trifluoroethyl)phosphite ($P(OCH_2CF_3)_3$) should be examined further. This compound has a relatively low cup-burner extinguishment concentration, although the boiling point is high. Tris(trifluoromethyl)phosphite ($P(OCF_3)_3$), if it can be made, is an ideal compound for evaluation. Others of particular interest are tris(pentafluoroethyl)phosphite ($P(OCF_2CF_3)_3$) and phosphites containing mixed $-CF_3$ and $-C_2F_5$ groups. The second most promising families are the phosphates with structures similar to those presented above for the phosphites, e.g., tris(trifluoromethyl)phosphate ($O{=}P(OCF_3)_3$) and tris(pentafluoroethyl)phosphate ($O{=}P(OCF_2CF_3)_3$). Finally, phosphites and phosphates with a bromine-containing alkyl group, e.g., (bromodifluoromethyl)bis(trifluoromethyl)phosphite ($P(OCF_3)_2(OCF_2Br)$) and (bromodifluoromethyl)bis(trifluoromethyl)phosphate ($O{=}P(OCF_3)_2(OCF_2Br)$) require investigation. Such compounds are expected to exhibit fire suppression synergism between the bromine and phosphorus. The list of promising phosphorus compounds is shown in Table 11.

A major problem is performing syntheses of the phosphate and phosphite esters of the types proposed. Phosphites can be easily synthesized by reaction of PCl_3 with ROH. These, in turn, can be oxidized to the phosphates. Unfortunately, alcohols that could be used to prepare esters containing fluorine bound to the carbon atom adjacent to oxygen are inherently unstable, breaking down by a 1,2-elimination of hydrogen fluoride (HF) to give carbonyl compounds. There may, however, be other ways to prepare such esters. One possibility is shown in Reaction 31 for tris(trifluoromethyl)phosphite.

$$P(OH)_3 + 3CF_3I \rightarrow P(OCF_3)_3 + 3HI \qquad (31)$$

Silicon compounds appear to offer relatively little promise. Silicon offers few inherent fire suppression capabilities due to the silicon itself, and many of the most interesting compounds (e.g., those containing bromofluoroalkyl and/or fluoroalkyl groups) are difficult to synthesize. Of particular concern is the instability of compounds containing -CF_3 groups immediately adjacent to the silicon atom, and such compounds are not considered here. Two silicon compounds do, however, offer promise at least for mechanistic studies if they can be prepared (Table 11). In these cases, -OR_f and/or -OCF_2Br groups are attached to the silicon atom. All of these are likely to have a low volatility and a high viscosity.

Amines, on the other hand, offer significant promise, particularly because a large amount of research is underway in Japan on the applications of fluoroalkyl amines as halon and CFC replacements. Note, however, that much of this research appears to be headed in the wrong direction. Much of it is on perfluoroalkyl amines, which are likely to have long atmospheric lifetimes. Nevertheless, the work provides synthetic routes and property evaluations. Compounds such as $N(CF_3)(CHF_2)(CF_2Br)$ could provide short atmospheric lifetimes and chemical suppression. A list of promising amines is shown in Table 11. Note that the first two listed (one of which was tested under the present program) are likely to have long atmospheric lifetimes; however, this needs to be investigated further.

A large amount of research is underway on fluoroethers as CFC replacements. The ether linkage provides a lower atmospheric lifetime only if it contains some hydrogen atoms. Work here and elsewhere indicates that in the absence of a bromine group, fluorinated ethers offer a fire suppression capability no higher than that of the hydrofluorocarbons and perfluorocarbons. Thus, there is little reason to pursue hydrofluoroethers or perfluoroethers further. Of interest, however, are hydrobromofluoroethers, and two such compounds are recommended in Table 11.

TABLE 11. FINAL LIST OF RECOMMENDED COMPOUNDS.

Formula	Name
Phosphorus Compounds	
$P(OCH_2CF_3)_3$	tris(2,2,2-trifluoroethyl)phosphite
$P(OCF_3)_3$	tris(trifluoromethyl)phosphite
$P(OCF_2CF_3)_3$	tris(pentafluoroethyl)phosphite
$P(OCF_3)_2(OCF_2Br)$	(bromodifluoromethyl)bis(trifluoromethyl)phosphite
$O{=}P(OCF_3)_3$	tris(trifluoromethyl)phosphate
$O{=}P(OCF_2CF_3)_3$	tris(pentafluoroethyl)phosphate
$O{=}P(OCF_3)_2(OCF_2Br)$	(bromodifluoromethyl)bis(trifluoromethyl)phosphate
Silicon Compounds	
$Si(OCF_3)_4$	tetrakis(trifluoromethyl)silicate
$Si(OCF_3)_3(OCF_2Br)$	(bromodifluoromethyl)tris(trifluoromethyl)silicate
$Si(OCH_2CF_3)_4$	tetrakis(2,2,2-trifluoroethyl)silicate
$Si(OCF_2Br)_4$	tetrakis(bromotrifluoromethyl)silicate
Bromofluoroamines	
$(CF_3)_3N$	tris(trifluoromethyl)amine
$(CF_3)_2(CF_3CF_2)N$	bis(trifluoromethyl)(pentafluoroethyl)amine
$(CBrF_2)(CHF_2)_2N$	(bromodifluoromethyl)bis(difluoromethyl)amine
$(CBrF_2)(CF_3)(CH_3)N$	methyl(bromodifluoromethyl)(trifluoromethyl)amine
$(CF_3)_2(CH_2CBrF_2)N$	bis(trifluoromethyl)(2-bromo-2,2-difluoroethyl)amine
$(CBrF_2)(CF_3)_2N$	bis(trifluoromethyl)(bromodifluoromethyl)amine
Fluoroethers	
CH_3-O-CF_2Br	methoxybromodifluoromethane
CF_2H-O-CF_2Br	difluoromethoxybromodifluoromethane

SECTION VII

RECOMMENDATIONS

Of the compounds examined in this project, future work should emphasize phosphites and, secondarily, amines. Of particular importance is the preparation, if possible, of $P(OCF_3)_3$. Dr. Jean'ne M. Shreeve at the University of Idaho could provide expertise in this area as well as in the preparation of other fluoroalkyl and bromofluoroalkyl compounds (both main group compounds and materials such as ethers), and the possibility of a collaborative arrangement will be examined.

Contacts have been made with Russian scientists, and these appear to offer good sources at reasonable cost for a number of materials of interest in this project and in future projects on main group compounds.

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APPENDIX A

FLUORINATED AMINES FROM CCOD

CCOD ID	Formula	Empirical formula	Molecular mass, amu	Boiling point, °C
		Nonbrominated Fluoroalkylamines		
922	$N(CF_3)_3$	C_3F_9N	221.03	-10
918	$N(CF_3)_2(CF_2CF_3)$	$C_4F_{11}N$	271.03	20.5
1315	$N(CF_3)(CF_2CF_3)_2$	$C_5F_{13}N$	321.04	46
991	$N(CF_2CF_3)_3$	$C_6F_{15}N$	371.049	70.3
1316	$N(CF_2CF_3)_2(CF_2CF_2CF_3)$	$C_7F_{17}N$	421.06	93
1317	$N(CF_2CF_3)(CF_2CF_2CF_3)_2$	$C_8F_{19}N$	471.06	114
1318	$N(CF_2CF_3)_2(CF_2CF_2CF_2CF_3)$	$C_8F_{19}N$	471.06	115
758	$N(CF_2CF_2CF_2CF_3)_3$	$C_{12}F_{27}N$	671.10	174
759	$N(CF_2CF_2CF_2CF_2CF_3)_3$	$C_{15}F_{33}N$	821.12	215
920	$N(CF_3)_2(CF{=}CF_2)$	C_4F_9N	233.04	13.7
1044	$N(CF_3)_2(CHF_2)$	C_3HF_8N	203.03	7.8
921	$N(CF_3)_2(CF_2CHF_2)$	$C_4HF_{10}N$	253.04	32
1010	$N(CF_3)_2(CH_2CF_3)$	$C_4H_2F_9N$	235.05	38
1006	$N(CH_3)(CF_3)_2$	$C_3H_3F_6N$	167.05	11.5
1009	$N(CF_3)_2(CH_2CHF_2)$	$C_4H_3F_8N$	217.06	51.35
1008	$N(CF_3)_2(CH_2CH_3)$	$C_4H_5F_6N$	181.08	33.29
1319	$N(CH_3)_2(CF_3)$	$C_3H_6F_3N$	113.08	20
1320	$N(CF_3)(CH_2CH_3)_2$	$C_5H_{10}F_3N$	141.14	71
1321	$-CH_2CH_2CH_2CH_2CH_2N(CF_3)-$	$C_6H_{10}F_3N$	153.15	107
1322	$-CH_2CH_2CH_2CH_2CH_2CH_2N(CF_3)-$	$C_7H_{12}F_3N$	167.17	133
1323	$N(CH(CH_3)_2)_2(CF_3)$	$C_7H_{14}F_3N$	169.19	109

APPENDIX A

FLUORINATED AMINES FROM CCOD (CONCLUDED)

CCOD ID	Formula	Empirical formula	Molecular mass, amu	Boiling point, °C
	Brominated Fluoroalkylamines			
990	$N(CBrF_2)(CF_3)_2$	C_3BrF_8N	281.93	40.6
919	$N(CF_3)_2(CF_2CF_2Br)$	$C_4BrF_{10}N$	331.94	60
1203	$N(CF_3)_2(CHFCF_2Br)$	C_4HBrF_9N	313.95	62.4
1204	$N(CF_3)_2(CF_2CHFBr)$	C_4HBrF_9N	313.95	74
1249	$N(CF_3)_2(CH{=}CHBr)$	$C_4H_2BrF_6N$	257.96	68.8
1200	$N(CF_3)_2(CHFCHBrF)$	$C_4H_2BrF_8N$	295.96	76.4
1053	$N(CF_3)_2(CH_2CBrF_2)$	$C_4H_2BrF_8N$	295.96	79.9
1202	$N(CF_3)_2(CH_2CH_2Br)$	$C_4H_4BrF_6N$	259.98	85.6
1209	$N(CF_3)_2(CF_2CFBrCF_3)$	$C_5BrF_{12}N$	381.95	82.2
1207	$N(CF_3)_2(CF_2CFClBr)$	C_4BrClF_9N	348.39	93.5
1208	$N(CF_3)_2(CFClCFClBr)$	$C_4BrCl_2F_8N$	364.85	125.6

APPENDIX B

FLUORINATED ETHERS FROM CCOD

CCOD ID	Molecular formula	Empirical formula	Boiling point, °C
No Chlorine or Bromine Atoms			
886	CF_3-O-CF_3	C_2F_6O	-59
890	CHF_2-O-CF_3	C_2HF_5O	-35
892	cyclo-O-$CF_2CF_2CF_2$-	C_3F_6O	-29.2
891	CF_3-O-CF_2CF_3	C_3F_8O	-23.3
	CH_3OCH_3	C_2H_6O	-24.8
887	CH_3-O-CF_3	$C_2H_3F_3O$	-24.2
1223	cyclo-CF_2-O-CF_2-O-CF_2-	$C_3F_6O_2$	-22.1
1334	CH_2F-O-CF_3	$C_2H_2F_4O$	-20
897	CF_3-O-CF_2-O-CF_3	$C_3F_8O_2$	-10.2
1034	CF_3CHF-O-CF_3	C_3HF_7O	-9.6
1246	CHF_2CF_2-O-CF_3	C_3HF_7O	-4.2
1248	CHF_2-O-CF_2CF_3	C_3HF_7O	0
691	CHF_2-O-CHF_2	$C_2H_2F_4O$	2
1259	cyclo-O-CF_2CHFCF_2-	C_3HF_5O	3.4
1314	CF_3CF_2-O-CF_2CF_3	$C_4F_{10}O$	5
1005	CH_3-O-CF_2CF_3	$C_3H_3F_5O$	5.59
1004	CF_3CH_2-O-CF_3	$C_3H_2F_6O$	5.69
1240	CH_3CH_2-O-CF_3	$C_3H_5F_3O$	6
1313	CF_3-O-$CF_2CF_2CF_3$	$C_4F_{10}O$	6.8
	CH_3-O-CH_2CH_3	C_4H_8O	7.4
1344	CF_3-O-CF_2CF_2-O-CF_3	$C_4F_{10}O_2$	16.7
1227	CHF_2CF_2-O-CF_2CF_3	C_4HF_9O	22
1011	CHF_2-O-$CHFCF_3$	$C_3H_2F_6O$	23.31
895	CHF_2-O-CH_2CF_3	$C_3H_3F_5O$	26.1
894	CF_3-O-$CH(CF_3)CH_3$	$C_4H_4F_6O$	27

APPENDIX B

FLUORINATED ETHERS FROM CCOD (CONTINUED)

CCOD ID	Molecular formula	Empirical formula	Boiling point, °C
No Chlorine or Bromine Atoms (continued)			
1014	CF_3CH_2-O-CF_2CF_3	$C_4H_2F_8O$	27.76
893	CHF_2-O-CF_2CHF_2	$C_3H_2F_6O$	28.5
1013	CH_3-O-$CF(CF_3)_2$	$C_4H_3F_7O$	29.35
809	CH_3-O-CH_2CF_3	$C_3H_5F_3O$	31.62
1012	CH_3-O-$CF_2CF_2CF_3$	$C_4H_3F_7O$	34.18
	CH_3CH_2-O-CH_2CH_3	$C_4H_{10}O$	34.5
1216	CHF_2-O-CF_2-O-CHF_2	$C_3H_2F_6O_2$	35
1345	CF_3-O-$CF_2CF_2CF_2CF_3$	$C_5F_{12}O$	36
1346	CF_3-O-$CF_2CF(CF_3)CF_3$	$C_5F_{12}O$	36
1003	CH_3-O-CF_2CHF_2	$C_3H_4F_4O$	37.19
1335	CF_3CHF-O-$CF_2CF_2CF_3$	$C_5HF_{11}O$	40.8
1040	CHF_2-O-$CH(CF_3)_2$	$C_4H_2F_8O$	42.1
1019	CHF_2-O-CF_2CH_2F	$C_3H_3F_5O$	43.1
593	CF_3CH_2-O-$CH{=}CH_2$	$C_4H_5F_3O$	43.7
1341	CHF_2-O-$CF(CH_3)CF_3$	$C_4H_4F_6O$	45
1023	CHF_2-O-$CH_2CF_2CF_3$	$C_4H_3F_7O$	45.9
1339	CH_3-O-$CH(CH_3)CF_3$	$C_4H_7F_3O$	47.8
1340	CHF_2-O-$CH(CH_3)CF_3$	$C_4H_5F_5O$	48
120	CF_3CH_2-O-CH_2CH_3	$C_4H_7F_3O$	50.3
1024	CH_3-O-$CH(CF_3)_2$	$C_4H_4F_6O$	51
1243	CH_2F-O-CF_2CHF_2	$C_3H_3F_5O$	53
1031	CF_3CH_2-O-CF_2CHF_2	$C_4H_3F_7O$	56.2
1217	CHF_2-O-CF_2CF_2-O-CHF_2	$C_4H_2F_8O_2$	58
913	$CF_3CF_2CF_2CF_2$-O-CH_3	$C_5H_3F_9O$	60
172	CHF_2CH_2-O-CH_2CH_3	$C_4H_8F_2O$	65

APPENDIX B

FLUORINATED ETHERS FROM CCOD (CONTINUED)

CCOD ID	Molecular formula	Empirical formula	Boiling point, °C
No Chlorine or Bromine Atoms (continued)			
1336	CH_3-O-$CH_2CF_2CHF_2$	$C_4H_6F_4O$	66
1218	CHF_2-O-CF_2-O-CF_2-O-CHF_2	$C_4H_2F_8O_3$	68
1022	CHF_2-O-$CH_2CF_2CHF_2$	$C_4H_4F_6O$	69
914	$CF_3CF_2CF_2CF_2$-O-CH_2CH_3	$C_6H_5F_9O$	73
1338	CHF_2-O-$CHFCF_2CHF_2$	$C_4H_3F_7O$	74
1219	CHF_2-O-CF_2-O-CF_2CF_2-O-CHF_2	$C_5H_2F_{10}O_3$	85
1220	CHF_2-O-CF_2CF_2-O-CF_2CF_2-O-CHF_2	$C_6H_2F_{12}O_3$	98
1094	cyclo-O-$CF(C_4F_9)CF_2CF_2CF_2$-	$C_8F_{16}O$	103
1221	CHF_2-O-CF_2-O-CF_2-O-CF_2CF_2-O-CHF_2	$C_6H_2F_{12}O_4$	110
1222	CHF_2-O-CF_2-O-CF_2-O-CF_2-O-CF_2CF_2-O-CHF_2	$C_7H_2F_{14}O_5$	130
Bromine-Containing			
1165	CH_3-O-CF_2CH_2Br	$C_3H_5BrF_2O$	[a]54.7
1162	CH_3-O-CF_2CHBr_2	$C_3H_4Br_2F_2O$	[b]55.8
1163	CH_3CH_2-O-CF_2CHBr_2	$C_4H_6Br_2F_2O$	[c]65
1166	CH_3CH_2-O-CF_2CH_2Br	$C_4H_7BrF_2O$	[d]70
1164	$CH_3CH_2CH_2$-O-CF_2CHBr_2	$C_5H_8Br_2F_2O$	[e]72.2
1342	CHF_2-O-CF_2CHBrF	$C_3H_2BrF_5O$	73
1160	$CH_3CH_2CH_2$-O-CF_2CHFBr	$C_5H_8BrF_3O$	[b]75.2
1170	CF_3-O-CH_2CH_2Br	$C_3H_4BrF_3O$	78.5
1343	CH_3-O-$CF(CF_3)CBrF_2$	$C_4H_3BrF_6O$	80
497	CH_3-O-CF_2CHBrF	$C_3H_4BrF_3O$	88.8
1148	$CF_3CBrFCH_2$-O-CH_2-O-$CH_2CBrFCF_3$	$C_7H_8Br_2F_8O_2$	[f]92
1158	CH_3CH_2-O-CF_2CHFBr	$C_4H_6BrF_3O$	106
1157	$CHFBrCF_2CH_2$-O-CH_3	$C_4H_6BrF_3O$	125

APPENDIX B

FLUORINATED ETHERS FROM CCOD (CONCLUDED)

CCOD ID	Molecular formula	Empirical formula	Boiling point, °C
	Bromine-Containing (concluded)		
1168	$CF_3CHBrCH_2$-O-$CH_2CHBrCF_3$	$C_6H_6Br_2F_6O$	167
1125	$CBrF_2CF_2CH_2CH_2CH_2CH_2$-O-$CH_2CH_3$	$C_8H_{13}BrF_4O$	185.7
1169	$CF_3CHBrCH_2$-O-CH_2-O-$CH_2CHBrCF_3$	$C_7H_8Br_2F_6O_2$	195
	Chlorine-Containing		
1049	CHF_2-O-$CHClCF_3$	$C_3H_2ClF_5O$	48.5
1048	CHF_2-O-CF_2CHClF	$C_3H_2ClF_5O$	56.5
1176	CF_3-O-CBrClCHBr-O-CF_3	$C_4HBr_2ClF_6O_2$	94.5
978	CH_3-O-CF_2CHCl_2	$C_3H_4Cl_2F_2O$	105

[a] 220 torr; [b] 130 torr; [c] 26 torr; [d] 175 torr; [e] 23 torr; [f] 28 torr