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FLUOROALKYL PHOSPHORUS COMPOUNDS

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Under the Montreal Protocol, an international treaty, the production of the fire and explosion protection agent Halon 1301 (bromotrifluoromethane, $CBrF_3$) was phased out in the United States at the end of 1993. No environmentally acceptable halon substitute that is equivalent to Halon 1301 in toxicity, effectiveness, and dimensionality has been identified. The objective of the overall effort is to assess fluoroalkyl-phosphorus compounds flame suppression performance. Prior studies have demonstrated that phosphorus based suppressants can have very effective flame suppression properties. The current study focused on overcoming two of the impediments (high boiling points and flammability) of the earlier studied compounds. The approach taken to both reduce boiling point and decrease flammability involves substitution of fluorine for hydrogen atoms. Additionally, this project sought to expand on this approach by exploring the fire suppression and physical properties of a broad range of phosphorus compound oxidation states and families (phosphonates, phosphites, phosphines).

14. SUBJECT TERMS
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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 Department of Defense, Strategic Environmental Research and Development Program (SERDP), under Defense Supply Service-Washington (DSS-W) Contract DASW01-01-P-0676, NMERI Number 8-34051. This Project is element 4D/14/1 under the Next-Generation Fire Suppression Technology Program (NGP).

The Start Date was 11 April 2001, and the End Date was 30 June 2002. The Technical Program Manager is Dr. Richard G. Gann, National Institute of Standards and Technology; the Contracting Officer's Technical Representative (COTR) is Dr. Ronald S. Sheinson, Naval Research Laboratory, and the NMERI Principal Investigator is Dr. J. Douglas Mather. Dr. Robert E. Tapscott served as the Deputy PI.

SUMMARY

A. TASK OBJECTIVE

The objective of this project was to expand on earlier promising evaluations of the potential of fluorinated alkyl phosphorus compounds to serve as fire extinguishants and replacements for halon 1301. Earlier halon replacement studies included a survey of "Main Group" compounds for their potential to serve as halon replacements. This study, among others, indicated promising fire suppression properties for alkylated phosphorus compounds. Two drawbacks, identified in these early studies, to implementation of alkyl-phosphorus compounds as fire suppressants were high boiling points (low vapor pressure) and the inherent flammability of the alkyl groups attached to the phosphorus.

This project was conceived in order to overcome both the boiling point and the flammability shortcomings through the incorporation of fluorinated alkyl groups as well as attempt to advance the study of the flame suppression properties of a wide range of fluorinated alkyl-phosphorus compounds. Sufficient fluorination of alkyl-phosphorus compounds was expected to result in reduced boiling points and reduction in inherent flammability of alkyl groups bonded to the phosphorus.

B. GENERAL METHODOLOGY

This project required the synthesis and cup-burner flame extinguishment evaluation of liquid or gaseous compounds from a wide variety of fluorinated alkyl-phosphines, alkyl-phosphonates, and alkyl-phosphites. A wide range of compounds was chosen for study to give a wide range of compound stabilities, toxicities, boiling points and flame suppressant performance. Based on the chemistry of phosphorus and the effects of heavily fluorinated alkyl substituents, such a broad study could identify potentially useful trends allowing further focusing of attention on specific compound types and structures having the desired chemical stability, flame suppression efficiency, and low boiling point. This report, which includes the objectives, methodology, results, important findings and conclusions, and implications for further research, is the final project deliverable. Of particular importance in this effort is an assessment of the potential of fluoroalkyl-phosphorus chemical sub-families and their derivatives to provide compounds as Halon 1301 substitutes and the development of a list of potential compounds.

C. TECHNICAL RESULTS

With essentially no exception, fluoroalkyl-phosphorus compounds are expected to be liquids at room temperature. While this is not a desirable property, the potential of fluoroalkyl-phosphorus compounds to be effective fire suppressants is well established. Indeed this limited study has identified compound(s) evidencing significantly enhanced flame suppression performance though it is not known whether the compound or its air breakdown product was responsible.

D. IMPORTANT FINDINGS AND CONCLUSIONS

Few halon replacement materials with potentially acceptable fire suppression performance, dimensionality, and physical (primarily, volatility) and toxicological properties have been identified. The lowest molecular weight main group families of compounds (i.e., the materials with the highest volatilities) often have hydrogen or halogen atoms directly attached to non-carbon atoms. The former (those containing hydrogen) are often flammable, and the latter (those containing halogens) are usually toxic (owing to hydrolysis). Both often have low stabilities. Moreover, few elements provide catalytic fire suppression capabilities, and compounds of most of those do not meet the requirements of this study. A major exception is fluoroalkyl phosphorus compounds, which hold significant promise despite their relatively low volatility.

E. SIGNIFICANT HARDWARE DEVELOPMENTS

The only hardware development made in this project involved incorporation of a heated nebulizer for sample dispersion as well as a method for preheating the air flow employed to disperse and fully evaporate the nebulized agent mist. These two modifications in conjunction with the use of a syringe pump for controlled introduction of the compound under test enabled the study of a broad range of compound boiling points, eliminated agent condensation concerns, enabled a very accurate characterization of agent/air concentrations, and yielded stable non-fluctuating agent/air mixtures for cup-burner evaluation study.

F. SPECIAL COMMENTS

None.

G. IMPLICATIONS FOR FURTHER RESEARCH

Fluoroalkylphosphorus compounds studied here have demonstrated a wide range of flame extinguishment performance, boiling point and air stability. Further select compounds (the trifluoromethyl phosphorus III derivatives) seem to evidence enhanced flame suppression properties. It can not be determined at this point whether the compound itself is responsible for the markedly effective flame suppression or whether the air break down products (alkyl-phosphorus oxides) are responsible for the improvement. What is apparent is that the actual air concentration of the active species is likely much lower than that listed for the test. It is possible that the effective species is present at a mere fraction of the stated 1.8% extinguishment concentration observed in flame suppression tests.

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LIST OF ABBREVIATIONS

CGET	Center for Global Environmental Technologies
COTR	Contracting Officer's Technical Representative
DEMP	diethyl methylphosphonate
DIMP	diisopropyl methylphosphonate
DMMP	dimethyl methylphosphonate
IMP	isopropyl methylphosphonate
ISO	International Standards Organization
MPA	methylphosphonic acid
NGP	Next-Generation Fire Suppression Technology Program
NIST	National Institute of Standards and Technology
NMERI	New Mexico Engineering Research Institute
SERDP	Strategic Environmental Research and Development Program
TFEP	tris(2,2,2-trifluoroethyl)phosphite
TMP	trimethylphosphate
USAF	United States Air Force

LIST OF UNITS AND SYMBOLS

C	concentration
K	Kelvin
P_b	external pressure at boiling point
p	vapor pressure
R	ideal gas constant
T	temperature
T_b	boiling point temperature
T_c	Trouton’s constant
Vol %	percent by gas volume
°C	degrees Celsius

SECTION I.
INTRODUCTION

A. OBJECTIVE

The objective was to evaluate the potential of compounds other than simple halocarbons and transition metal compounds as replacements for halon fire extinguishing agents. Only compounds that are not solids at room temperature and are representative of the broad range of oxidation states of phosphorus are targeted.

B. SCOPE

This project requires the assessment of liquid compounds of the fluoroalkyl-phosphorus chemical family as halon replacements. Of particular importance is an assessment of the relative ability of phosphorus III and V compounds as represented by a range of phosphonates and phosphite compounds to provide flame extinguishment and ultimately serve as Halon 1301 substitutes. The compounds studied were intended to serve as a survey of the performance of this general family of compounds with expectation that a refined set of fluoroalkyl-phosphorus compounds identified later in this report would subsequently be acquired and tested.

C. APPROACH

Much of the information acquired in earlier studies of the flame suppressing properties of organophosphorus compounds was employed is the selection of an initial list of fluoroalkyl-phosphorus compounds for synthesis and cup-burner testing. The compounds selected for synthesis were prepared under subcontract to the University of Idaho and were tested for their cup-burner flame extinguishment at the New Mexico Engineering Research Institute located at the University of New Mexico .

D. BACKGROUND

Past work under the United States Air Force (USAF) and the Advanced Agent Working Group (AAWG) performed an brief assessment of the fire suppressant potential of compounds in a number of elemental families [1]. As a result of this initiative, it was recommended that tropodegradable bromocarbons [2], silicon compounds [3], phosphorus compounds [4], and metal compounds [5] receive particular attention. The study of phosphorus based suppressants was extended further in NGP sponsored research which demonstrated the effectiveness of certain phosphorus based compounds to act as flame extinguishants. Moreover, significant past work under the Next-Generation Fire Suppression Technology Program (NGP) has been performed on phosphorus compounds as well as amines, ethers, and silicon compounds [6, 7].

This project represents a much needed examination of a broad range of fluoro-phosphorus compounds with emphasis on heavily fluorinated phosphonates and phosphite chemical structures.

Some results from this present project have been reported at the recent HOTWC 20003 conference [8].

SECTION II.

FLUOROALKYL PHOSPHORUS COMPOUNDS: SELECTION ACQUISITION AND TESTING

A. PHOSPHORUS COMPOUND EXTINGUISHMENT STUDIES

1. Suppression effectiveness

A review of the proposed extinguishment mechanisms and testing of phosphorus compounds has been presented [7]. In addition, several reports addressing the combustion or oxidative chemistry and flame extinguishment performance of alkyl phosphorus compounds have appeared.

In work sponsored by the Next-Generation Fire Suppression Technology Program, research efforts at the New Mexico Engineering Research Institute extended earlier promising studies on alkyl phosphorus compound flame extinguishment performance to the study of several new partially and fully fluorinated alkyl phosphorus compounds from the phosphine and phosphonate families[9].

Researchers have demonstrated that phosphorus compounds appear to provide a chemical fire extinguishment mechanism, and in fact some appear to be highly effective flame extinguishants. Much reported work has been performed on dimethyl methyl phosphonate (DMMP) and related compounds [15,10]. Though DMMP shows very promising flame suppression characteristics, this compound and most of the related compounds studied to date have serious practical drawbacks. Specifically, most of the standard phosphorus compounds studied to date are flammable and have low vapor pressures[11-14].

For phosphorus based compounds to be employed as fire extinguishant compounds effective nonflammable and lower boiling structures needed to be identified.

The introduction of one or more polyfluoroalkyl or polyfluoroalkoxy moieties, e.g., $[O{=}P(OCH_3)_{2-n}(OCF_3)_n CH_3]$ (n = 1, 2) or $[O{=}P(OCH_3)_2CF_3]$ offers an opportunity to minimize or possibly eliminate both of these unfavorable properties. Of particular initial interest for testing is the totally fluorinated trimethoxy phosphonate $O{=}P(OCF_3)_3$, which has a boiling point of 52 ºC [11].

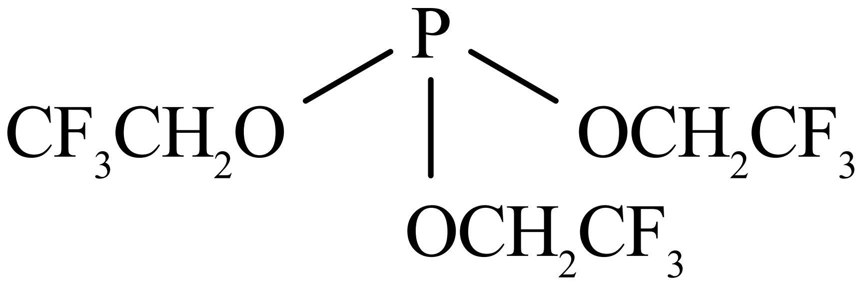
A kinetic model has been developed for the combustion chemistry of dimethyl methylphosphonate (DMMP, CCOD ID 1375, $O{=}P(CH_3)(OCH_3)_2$) [12]. The opposed-jet burner has been shown to be effective for studying this low-volatility compound [13], and studies with this apparatus have shown that DMMP is a better suppressant when introduced in the oxidizer stream [14] and that DMMP and trimethylphosphate (TMP, CCOD ID 1225, $O{=}P(CH_3)_3$) are approximately forty times more effective than nitrogen on a per-mole basis in suppressing flames and two to four times more effective than Halon 1301 [15]. Like Halon 1301, the effectiveness is greater when DMMP is introduced on the oxidizer side, rather than the fuel side, of non-premixed flames even when the amounts actually reaching the flame are taken into account [16]. This behavior is not observed with argon, which has no chemical contribution to flame suppression.

Gas-phase studies in nitrogen show that diethyl methylphosphonate (DEMP, $O{=}P(CH_3)(OCH_2CH_3)_2$) pyrolyzes to form ethene ($CH_2{=}CH_2$), ethanol (CH_3CH_2OH), and ethyl methylphosphonate ($O{=}P(OH)(CH_3)(OCH_2CH_3)$) [17]. Formation of ethene may result from formation of a six-membered ring transition state or by scission of a $PO{-}CH_2CH_3$ bond with subsequent loss of a hydrogen atom from the ethyl radical ($\bullet CH_2CH_3$). Similar results have been found in pyrolysis studies of diisopropyl methylphosphonate (DIMP), which gives propene ($CH_2{=}CHCH_3$), 2-propanol ($CH_3CH(OH)CH_3$), isopropyl methylphosphonate (IMP, $O{=}P(OH)(CH_3)(OCH(CH_3)_2)$), and methylphosphonic acid (MPA, $O{=}P(OH)_2(CH_3)$) [18]. A six-membered ring transition state is proposed for formation of 2-propene. Derivatization followed by gas chromatography/mass spectrometry has identified DMMP, methyl methylphosphonate ($O{=}P(OH)(CH_3)(OCH_3)$), dimethyl phosphate ($O{=}P(OH)(OCH_3)_2$), monomethyl phosphate ($O{=}P(OH)_2(OCH_3)$), MPA, orthophosphoric acid ($O{=}P(OH)_3$), phosphorous acid ($P(OCH_3)_3$), and phosphonic acid ($O{=}PH(OH)_2$) as combustion products in a $CH_4/O_2/N_2$ flame doped with DMMP [19].

Based on opposed-flame burner results, there has been significant interest in DMMP as a potential fire extinguishing material. No cup burner values have, however, been determined for DMMP and it would be difficult to obtain such values because of its very high boiling point (181 °C, [20]) and low vapor pressure (1.2 Torr at 25 °C, [21]). Attempts to determine a cup burner extinguishment concentration for a higher volatility non-fluorinated compound, trimethyl phosphite ($P(OCH_3)_3$), has also been unsuccessful, due, in this case, to its flammability. All of the phosphorus compounds discussed above in this section are, in fact, flammable.

There are two ways around the flammability problem. One is to blend the material with a nonflammable carrier; the other is to work with fluorinated alkyl derivatives of phosphorus. Cup burner testing using both of these approaches has been carried out and the results are presented in this report.

Prior work has shown that the compound tris(2,2,2-trifluoroethyl)phosphite (**1**), TFEP (boiling point of 130 to 131 °C at 743 Torr [22]) exhibits a particularly low cup-burner extinguishment concentration [7]. More recent studies yielded an extinguishing concentration of 1.69 vol% for *n*-heptane fuel. Based on these results the lower molecular weight tris(trifluoromethyl)phosphite (**2**) or tris(trifluoromethyl)phosphate (**3**), were seen as promising materials for future study. Both of these compounds are expected to be lower in boiling point than tris(2,2,2-trifluoroethyl)phosphite (1). The effects of fluorination are generally expected to reduce the flammability of the alkyl substituents, however, phosphorus +3 phosphite and phosphine compounds can be air sensitive to a degree and so fluorination can lead to increased air reactivity. The phosphonates (P=O) structures are not affected in this manner as the phosphorus oxidation state is already +5.



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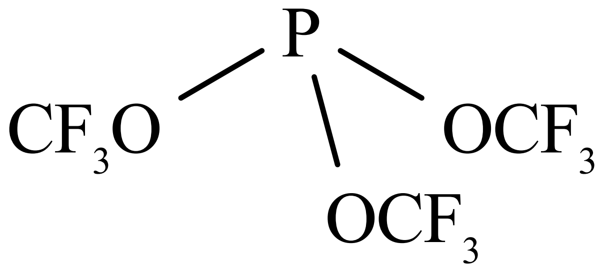

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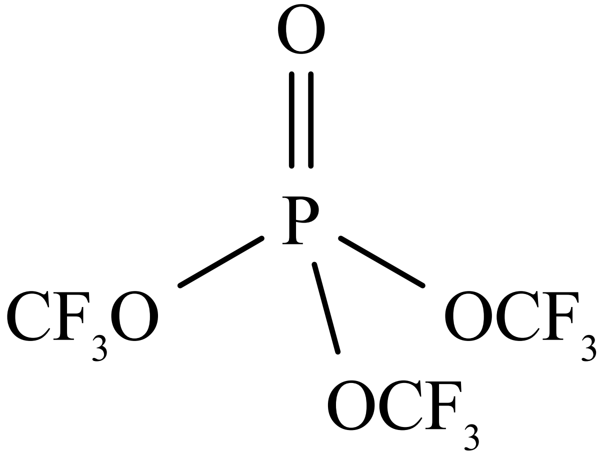

(3)

Tris(trifluoromethyl)phosphite ($P(OCF_3)_3$) has not been reported; however, tris(trifluoromethyl)phosphate ($O=P(OCF_3)_3$) has been prepared by oxidation of tris(trifluoromethyl)phosphine ($P(CF_3)_3$ [23]. The phosphate has a boiling point of 52 °C at 760 Torr pressure and a melting point of -86 °C. The vapor pressure p in Torr can be fit to the equation $\log_{10}p = -1445/T + 7.33$, where T is in units of K, corresponding to a Trouton's Constant of 85.22 J/mol-K. This equation gives a calculated vapor pressure of 304 Torr at 25 °C.

This project was conceived to further investigate the potential of phosphorus based compounds to perform as fire suppressants and to advance the understanding of the effects of the diverse structural chemistry on the flame suppression process. Following the identification of eight promising fluoroalkyl- and hydrofluoroalkyl-substituted phosphorus compounds and their synthesis in the laboratory of Dr. Jean'ne Shreeve at the University of

Idaho, seven of the eight fluoroalkyl and hydrofluoroalkyl phosphorus compounds were ultimately evaluated for their flame extinguishment performance using the NMERI Cup-burner. This work is presented in full below.

B. FLUOROALKYL PHOSPHORUS COMPOUNDS - ACQUISITION AND CHARACTERIZATION

A number of compounds of silicon, phosphorus, and other materials based on chemical elements other than carbon have been examined as fire extinguishants and possible replacements for Halon 1301[24]. Of particular interest have been compounds of phosphorus [9]. Phosphorus compounds appear to provide a chemical fire extinguishment mechanism, and some appear to be highly effective [7].

Phosphorus compounds show extraordinary effectiveness as flame extinguishants, and there is evidence for a chemical mechanism. Most work to date, however, has emphasized alkyl phosphonates and other nonhalogenated phosphorus-containing esters or phosphonitriles. The former compounds are often flammable and both types of compounds have low volatilities. Incorporation of fluorine in the alkyl structures appeared to be a viable approach to reducing compound boiling point and decreasing flammability. The effect of fluorine on toxicities of the phosphorus compounds, however, is unknown.

One way to address both problems of flammability and low volatility is to work with phosphorus compounds containing fluoroalkyl or hydrofluoroalkyl groups. Incorporating fluorinated alkyl groups potentially decreases boiling points and simultaneously reduces compound flammability. For example, tris(2,2,2-trifluoroethyl)phosphite ($P(OCH_2CF_3)_3$,TFEP) has a cup burner extinguishment concentration of 1.78 vol.% for *n*-heptane fuel [7]. This can be compared with the concentration of approximately 3 vol% for Halon 1301. TFEP has a normal boiling point of approximately 131° C compared to 181° C for DMMP and is non flammable.

There is still, however, a major problem with TFEP. Though the volatility is improved, it is still not nearly what one would like for application as a fire suppressant. For that reason, one needs to examine fluoroalkyl phosphorus compounds with lower molecular weights. The compound $O=P(OCF_3)_3$, tris(trifluoromethyl)phosphonate, has been reported to have a normal boiling point of 52 C. The hypothetical compound $P(OCF_3)_3$, tris(trifluoromethyl)phosphite may also have a low boiling point.

Several phosphonates and phosphines (+5 and +3 oxidation states, respectively) containing fluoroalkyl and hydrofluoroalkyl groups, were identified for acquisition based on predictions of the success of available synthetic methods. Expectations of non-flammability due to replacement of alkyl hydrogen's with fluorine in these new compounds were balanced by a recognition that increased fluorination could well result increased instability to air.

1. Compound selection

Compound selection guidelines were identified to rule out compounds likely to be flammable, susceptible to hydrolysis, or toxic. Compounds such as PH_3 or $P(CH_3)_3$ were ruled out as being flammable while compounds involving P-F bonds were ruled out due to expected hydrolysis and unacceptable toxicity.

Fluoroalkyl and hydrofluoroalkyl phosphorus compounds containing substituent groups $-CF_3$, $-CF_2H$, $-CH_2CF_3$, $-CF_2CH_2F$, $-CF_2CF_3$, and/or related structural isomers were identified as unlikely to suffer the problems of flammability, hydrolysis and toxicity while possibly achieving the lower boiling points desired. These expectations were not fully realized as will be described further on in this report. The compounds selected for synthesis are listed in Table 1.

TABLE 1. COMPOUNDS SELECTED FOR SYNTHESIS

#	Compound	Formula
1	Tris(trifluoromethyl) phosphonate	$O=P(CF_3)_3$
2	Bis(trifluoromethyl)methoxy phosphine	$P(OCH_3)(CF_3)_2$
3	Tris(2,2,2-trifluoroethoxy) phosphite	$P(OCH_2CF_3)_3$
4	Bis(trifluoromethyl) trifluoromethoxy phosphonate	$O=P(OCH_3)(CF_3)_2$
5	Bis(2,2,2-trifluoroethoxy) trifluoromethyl phosphine	$P(OCH_2CF_3)_2CF_3$
6	Bis(trifluoromethyl) 2,2,2-trifluoroethoxy phosphine	$P(OCH_2CF_3)(CF_3)_2$
7	Bis(trifluoromethyl) 2,2,2-trifluoroethoxy phosphonate	$O=P(OCH_2CF_3)(CF_3)_2$
8	Tris(trifluoromethoxy) phosphonate	$O=P(OCF_3)_3$

The compounds listed represent a range of related structures and include both phosphine and phosphonate compounds. Including in the study both P(III) and P(V) phosphorus oxidation states as well as incorporating, where possible, similar fluorinated substituents increases the probability of identifying promising chemical families. Promising compounds would serve as guides to future research and compound synthetic efforts.

2. Synthetic methods and results

The compounds were synthesized utilizing bench top and vacuum line procedures. Each of the products was purified and then characterized, as needed for structure verification, by ^{19}F, ^{31}P and ^{13}C NMR, infrared and mass spectral measurements and by elemental analysis. The syntheses performed as well as relevant literature references are briefly described below.

Compound 1, synthesis of tris(trifluoromethyl)phosphonate, $O=P(CF_3)_3$. This two step synthesis involved reaction of red phosphorus with CF_3I forming the flammable intermediate $(CF_3)_3P$ followed by an oxidation insertion reaction with nitrous oxide and nitrogen dioxide to form the phosphonate, $(CF_3)_3P=O$ [7]. These steps are described in Reactions 1 and 2 below.

Reaction 1. Step 1: Synthesis P(CF3)3 intermediate

$$\text{Red Phosphorus} + CF_3I \xrightarrow{232° \text{ C, 60hr}} P(CF_3)_3 \quad \text{(52\% yield)}$$

Reaction 2. Step 2:Oxidative conversion to O=P(CF3)

$$P(CF_3)_3 \xrightarrow{NO_2} (CF_3)_3P{=}O \quad \text{(100 \% yield)}$$

Compound 2, synthesis of bis(trifluoromethyl)methoxyphosphine, $(CF_3)_2POCH_3$. The intermediate, $(CF_3)_2PI$, formed as one of the products in 25% yield from the reaction of CF_3I and red phosphorus were reacted at 25 ˚C with AgCl to form $(CF_3)_2PCl$ in an approximate 100% yield. The chloride was subsequently reacted with methanol in the presence of triethyl amine [7] substituting the methoxide for the chlorine. These reactions are summarized in Reaction 3 below.

Reaction 3. Methanol replacement of Cl

$$(CF_3)_2PCl \xrightarrow[(CF_3CH_2)_3N]{CH_3OH} (CF_3)_2POCH_3 \quad \text{(85\% yield)}$$

Compound 3, synthesis of tris(2,2,2-trifluoroethoxy)phosphite, $P(OCH_2CF_3)_3$. The synthesis of $P(OCH_2CF_3)_3$ was carried out by adding trifluoroethanol dropwise into a vigorously stirred solution of phosphorus trichloride (slight excess) at 0˚C. After five hours, fractional distillation gave the desired product. These reactions are summarized in Reaction 4 below.

Reaction 4. Conversion of the chlorophosphine to trifluoroethoxide

$$PCl_3 + CF_3CH_2OH \xrightarrow{\qquad} P(OCH_2CF_3)_3 \quad \text{(100\% yield)}$$

Compound 4, synthesis of bis(trifluoromethyl) trifluoromethoxyphosphonate $O{=}P(OCH_3)(CF_3)_2$. The $(CF_3)_2POCF_3$ intermediate was oxidized with a slight molar deficiency of nitrogen dioxide as in Synthesis l. The NO was removed under vacuum. This reaction is summarized in Reaction 5 below.

Reaction 5. Oxidation to Phosphonate

$$(CF_3)_2POCF_3 \xrightarrow{NO_2} (CF_3)_2P(O)OCH_3$$ (100% yield)

Compound 5, synthesis of bis(2,2,2-trifluoroethoxy) trifluoromethylphosphine, $(CF_3)P(OCH_2CF_3)_2$. This synthesis is very similar to the synthesis of **Compound 2** above. This reaction is summarized in Reaction 6 below.

Reaction 6. Conversion to fluoroalkoxide

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

Compound 6, synthesis of bis(trifluoromethyl) 2,2,2-trifluoroethoxyphosphine, $(CF_3)_2POCH_2CF_3$: This synthesis is very similar to Synthesis 2 above. This reaction is summarized in Reaction 7 below.

Reaction 7. Conversion to fluoroalkoxide

$$(CF_3)_2PCl \xrightarrow[(CF_3CH_2)_3N]{CF_3CH_2OH} (CF_3)_2POCH_2CF_3$$

Compound 7, synthesis of bis(trifluoromethyl) 2,2,2-trifluoroethoxyphosphonate, $(CF_3)_2P(O)OCH_2CF_3$. This synthesis is very similar to Synthesis 4 above. This reaction is summarized in Reaction 8 below.

Reaction 8. Conversion to fluoroalkoxide

$$(CF_3)_2POCH_2CF_3 \xrightarrow{NO_2} (CF_3)_2P(O)OCH_2CF_3$$

Compound 8, attempted synthesis of tris(trifluoromethoxy)phosphonate, $(CF_3O)_3P{=}O$. This synthesis attempt was unsuccessful but employed a strategy similar to that used in the successful preparation of **Compound 1**. The Reaction attempted is outlined in Reaction 9 below [23].

Reaction 9, Attempted oxidation of $(CF_3)_3P$.

$$(CF_3)_3P \xrightarrow{O_2} (CF_3O)_3P{=}O \quad \text{(no isolable product)}$$

The synthetic products of the above reaction are summarized in Table 2. Final product weights and boiling points are listed.

TABLE 2. SYNTHETIC RESULTS

#	**Compound - Formula**	**Boiling Point ºC**	**Synthetic product weight (g)**
1	Tris(trifluoromethyl) phosphonate $O{=}P(CF_3)_3$	32 ºC	7.3
2	Bis(trifluoromethyl)methoxy phosphine, $P(OCH_3)(CF_3)_2$	55 ºC	5.3
3	Tris(2,2,2-trifluoroethoxy) phosphite, $P(OCH_2CF_3)_3$	130 ºC @ 743 mm	50.0
4	Bis(trifluoromethyl) trifluoromethoxy phosphonate, $O{=}P(OCH_3)(CF_3)_2$	42 ºC @ 745 mm	5.5g
5	Bis(2,2,2-trifluoroethoxy) trifluoromethyl phosphine, $P(OCH_2CF_3)_2CF_3$	111º C	7.2
6	Bis(trifluoromethyl) 2,2,2-trifluoroethoxy phosphine, $P(OCH_2CF_3)(CF_3)_2$	25 ºC @ 50mm	6.5
7	Bis(trifluoromethyl) 2,2,2-trifluoroethoxy phosphonate, $O{=}P(OCH2CF_3)(CF_3)_2$	130 ºC (estimate)	7.0
8	Tris(trifluoromethoxy) phosphonate, $O{=}P(OCF_3)_3$	52º C	Not synthesized

3. Cup-Burner flame extinguishment testing

Cup burner evaluation and air stability observations were performed at the University of New Mexico. The University currently operates two different cup burners, the NMERI Standard Cup Burner and the larger ISO Cup Burner. The smaller NMERI Standard Cup Burner was employed for this project due to the reduced requirement for agent for testing. Due to the limited amount of compound prepared (5 to 10 grams), the cup-burner methodology employed provides an upper bound extinguishment concentration which is expected to be slightly higher than the actual minimum extinguishment concentration.

In view of the wide range of boiling points represented by the compounds synthesized, a means for preventing the condensation on to cooler surfaces and countering the evaporative cooling effects of the nebulized agent as it is dispersed into the air stream of the cup-burner was required. These issues were addressed using a preheater for the inlet air stream as depicted in Figures 1 and 2. Heating the inlet air to between 50 and 55 ºC counteracted the evaporative cooling effects of the misted agent at the tip of the nebulizer and enhanced droplet vaporization. On mixing with the cooler nebulized agent/air stream, the column temperature drops to between 45 to 50 ºC. The preheated air was also employed to warm the entire cup-burner chimney prior to a test run and as a result no condensation of agent was observed during or following extinguishment testing. Extinguishment testing results are summarized in Table 3.

All compounds tested were shipped and stored in sealed glass vials prior to use and were tested immediately on opening. Generally opening the vials and exposing the liquid contents to air was not particularly remarkable, Table 4. However, in two cases the compounds reacted quite vigorously on air exposure. Extremely vigorous reaction on air exposures occurred for compound 2, bis(trifluoromethyl)methoxy phosphine, $P(OCH_3)(CF_3)_2$, and compound 6, bis(trifluoromethyl) 2,2,2-trifluoroethoxy phosphine, $P(OCH_2CF_3)(CF_3)_2$, on breaking open their respective glass sealed vials. This reaction occurred as air entered and contacted the liquid agent. It seems very likely that both compounds would react, at least partially, to form unknown products prior to entering the flame zone. For each compound extinguishment testing started at air concentrations of 5 vol. % and followed by retests at progressively lower air concentrations until either the sample of test compound was exhausted or extinguishment failed to occur.

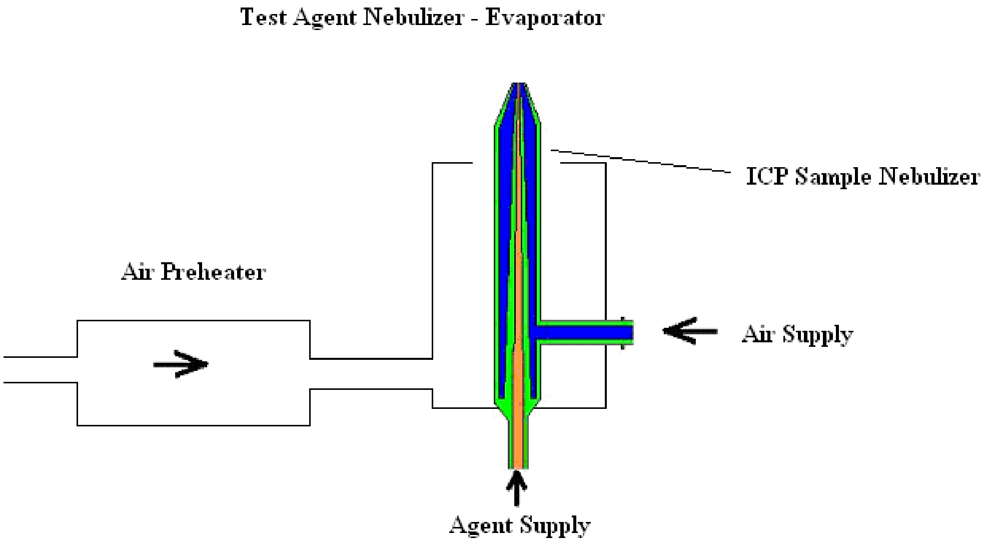

Figure 1. Sample nebulizer and air pre-heater.

The nebulizer employed in this apparatus is a standard feature in all atomic emission inductively coupled spectrometers. These devices readily aspirate samples at rates of 1 to 3 cc per minute at air pressures of ~40psig. They can also be forced to higher levels of output by employing a syringe pump or similar device. Two air flows are employed in this experimental setup. The first aspirates the sample and the second provides a makeup air flow bringing the total air flow to nominally 10 l/min. in the cup-burner. Air requirements were met using a regulated air flow from a storage tank supplied in turn by an oil-less 3 hp compressor. Air flows were set and monitored using a mass flow meter.

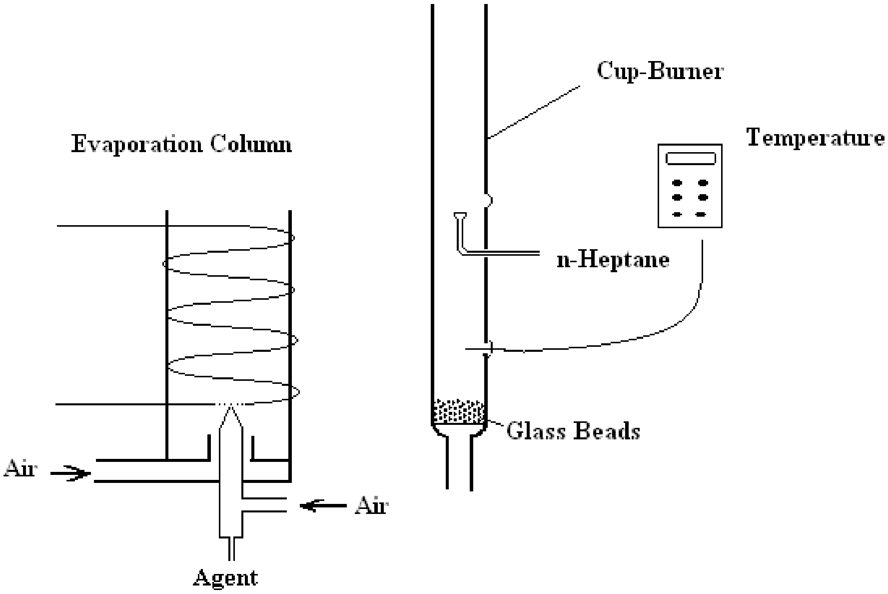

Figure 2. Cup-burner equipped with sample nebulizer and evaporation column.

TABLE 3. SUMMARY OF CUP-BURNER EXTINGUISHMENTS

#	Compound, Formula	Cup-burner Testing
1	Tris(trifluoromethyl) Phosphonate, $O{=}P(CF_3)_3$	No flame lift-off or extinguishment @ 5%
2	Bis(trifluoromethyl)methoxy Phosphine, $P(OCH_3)(CF_3)_2$	Spontaneously ignites on exposure to air *
3	Tris(2,2,2-trifluoroethoxy) Phosphite, $P(OCH_2CF_3)_3$	3.1%
4	Bis(trifluoromethyl) trifluoromethoxy Phosphonate, $O{=}P(OCH_3)(CF_3)_2$	4.6%
5	Bis(2,2,2-trifluoroethoxy) trifluoromethyl Phosphine, $P(OCH_2CF_3)_2CF_3$	3.0%
6	Bis(trifluoromethyl) 2,2,2-trifluoroethoxy Phosphine, $P(OCH_2CF_3)(CF_3)_2$	1.8%
7	Bis(trifluoromethyl) 2,2,2-trifluoroethoxy Phosphonate, $O{=}P(OCH2CF_3)(CF_3)_2$	Lift-off but no extinguishment @ 5%
8	Tris(trifluoromethoxy) Phosphonate, $O{=}P(OCF_3)_3$	Not synthesized

*Note: In view of the low cup-burner test value of **Compound 6**, the structurally similar **Compound 2** was preserved in order to provide a future opportunity to identify the product of its reaction with air.

Air sensitivity evidenced by a fuming reaction on exposure to air was observed in most but not all cases. These observations were made on opening the sealed glass vials all compounds were shipped and stored in. In view of the low cup-burner test value of compound 6, the structurally similar **Compound 2** was preserved in order to provide an opportunity to identify the product of its reaction with air. It is likely that **Compound 6** undergoes an air oxidation to yield a phosphonate structure $O{=}P(OCH_2CF_3)(CF_3)_2$. Air reactivity observations are summarized in Table 4.

TABLE 4. AIR REACTIVITY OBSERVATIONS

#	Compound - Formula	Observations on exposure of test agent to air
1	Tris(trifluoromethyl) phosphonate $O=P(CF_3)_3$	No white fumes, does not ignite cloth
2	Bis(trifluoromethyl)methoxy phosphine, $P(OCH_3)(CF_3)_2$	White fumes, ignites spontaneously
3	Tris(2,2,2-trifluoroethoxy) phosphite, $P(OCH_2CF_3)_3$	No fumes, no ignition
4	Bis(trifluoromethyl) trifluoromethoxy phosphonate, $O=P(OCH_3)(CF_3)_2$	Some fumes, no ignition
5	Bis(2,2,2-trifluoroethoxy) trifluoromethyl phosphine, $P(OCH_2CF_3)_2CF_3$	Some fumes, no ignition
6	Bis(trifluoromethyl) 2,2,2-trifluoroethoxy phosphine, $P(OCH_2CF_3)(CF_3)_2$	Ignites cloth, no spontaneous ignition, fumes strongly
7	Bis(trifluoromethyl) 2,2,2-trifluoroethoxy phosphonate, $O=P(OCH2CF_3)(CF_3)_2$	No white fumes, does not ignite cloth
8	Tris(trifluoromethoxy) phosphonate, $O=P(OCF_3)_3$	Not synthesized

C. OBSERVATIONS AND CONCLUSIONS

Phosphonates P(V) having only $-CF_3$ groups are possibly too stable to react in flame. When compound 1, tris(trifluoromethyl)phosphonate $O=P(CF_3)_3$, was tested at 5 vol. % no evidence of flame lift-off was observable. **Compound 4**, a phosphonate, showed lift-off and flame extinguishment well below 5 vol. %. **Compound 7**, also a phosphonate, showed lift-off but no flame extinguishment at 5 vol. %. Limited data (**Compounds 1, 4, and 7**) also suggest that phosphonates may need sufficient hydrogen atoms in their structures to enable compound break down in the flame zone in order to become chemically active as combustion suppressants.

Only **Compound 4** approached the desired boiling point range. In the trade-off between higher degrees of fluorination to reduce the boiling point and moderate hydrogenation for decomposition and efficient fire suppression there are limited chemical options and therefore there may limited further promise in this family of compounds. This conclusion must be tempered by the observed low cup-burner test value (1.8%) of **Compound 6** and the tentative conclusion that it is likely that air reaction is converting it to a very efficient flame suppressant. It can not, however, be concluded at this point that the air oxidation produces a complete conversion to a single compound or that the reaction is complete by the time the products enter the flame zone.

The more volatile phosphine P (III) compounds with -CF_3 groups tend to be spontaneously flammable while those with fluoroethoxy groups were relatively stable (**Compound 3**). Phosphines in general span a wide range of air (O_2) reactivities. Some are air stable while other are quite air reactive. $P(CF_3)_3$ is known to spontaneously ignite on air exposure while trimethylphosphine - $P(CH_3)_3$ is relatively air stable. Phosphorus +3 fluoroalkyls (**Compounds 2** (bis(trifluoromethyl)methoxyphosphine, $P(OCH_3)(CF_3)_2$), **3** (tris(2,2,2-trifluoroethoxy) phosphite, $P(OCH_2CF_3)_3$), **5** (bis(2,2,2-trifluoroethoxy) trifluoromethyl-phosphine, $P(OCH_2CF_3)_2CF_3$), and **6** (bis(trifluoromethyl) 2,2,2-trifluoroethoxyphosphine, $P(OCH_2CF_3)(CF_3)_2$)) illustrate this range of air reactivities. While the higher boiling compounds clearly are not of practical value by themselves for aircraft application, they could be incorporated in solid propellant gas generation devices where adequate heat is available to fully vaporize, disperse, and possibly initiate the thermal breakdown of the compound. The possibility that some of these compounds decompose on air exposure to yield highly effective flame extinguishants is tantalizing and the opportunity to implement such compounds with gas generating dispersion aids may well be worth investigation. Compounds with higher volatility (higher fluorine content) tend toward spontaneous flammability.

Finally, in earlier work, tris(2,2,2-trifluoroethoxy)phosphine ($P(OCH_2CF_3)_3$,TFEP) had been reported to have a cup burner extinguishment concentration of 1.78 vol.% for *n*-heptane fuel [7]. This value is much lower than that observed here, and differences in manner of sample vaporization could well be responsible. In the earlier studies, a hot sand bath (>250° C) was employed to volatilize the compound as it was introduced into the base of the cup-burner. It is possible this method induced thermal decomposition and air reaction of the test compound yielding a more effective flame suppressant.

D. RECOMMENDED STUDIES

Several directions for further work in this area present themselves. While the testing reported here exposed real limitations to phosphorus compounds as fire suppressants it also provided, as initially hoped, a basis for more focused research of promising compound structural areas.

Compound 6, though air reactive, yielded on testing, an impressively low cup-burner value. It is possible this low cup-burner value was due to a break down product whose air concentration is actually significantly lower than 1.8%. Identification and study of **Compound 6** (or **Compound 2**) air reaction products may lead to significant advancements in phosphorus-based suppressants for aircraft applications. A compound that can be easily dispersed as a gas or vapor and which subsequently decomposes to form a highly effective flame extinguishant may have some applicability to aircraft dry bays and other unoccupied areas. It may be that the required extinguishing concentration of such an agent could be in the 1% or lower range. The nature and toxicity of **Compound 6** air decomposition products needs to be determined.

The break down products of **Compound 2** (bis(trifluoromethyl)methoxy-phosphine, $P(OCH_3)(CF_3)_2$)are likely to be similar to those of **Compound 6** are predicted to be oxidation products containing P=O and P-O-fluoroalkane groups. Some of these compounds might (as indicated by **Compound 4's** 42° C boiling point) border on acceptability for aircraft applications. Additional effort directed to the acquisition of fluoro-phosphorus compounds similar to $P(OCH_3)(CF_3)_2$ with $-OCFH_2$ instead of $-OCH_3$ is indicated.

The synthesis of **Compound 8** (tris(trifluoromethoxy)phosphonate, $O=P(OCF_3)_3$) has been reported in the literature [23]. While this projects synthesis attempt of $O=P(OCF_3)_3$) was unsuccessful, a realistic expectation of **Compound 8's** acquisition still exists. The 52° C boiling point of **Compound 8** as well as its similarity to the structures thought to be the breakdown products from **Compound 6**, that may be contributing to its demonstrated higher effectiveness, make **Compound 8** a prime target for a further acquisition and testing effort;

Synthesis and testing of compounds where hydrogen substituted CF_2H or CFH_2 groups replace CF_3 may over come the apparent lack of reactivity of compound 1, $O=P(CF_3)_3$

which could possibly have prevented breakdown in the flame zone and failure to act as a flame extinguishant at the 5% initial test concentration.

These recommended compounds are summarized below

TABLE 5. COMPOUNDS FOR FUTURE STUDY

Phosphorus III compounds	**Phosphorus V compounds**
$P(OCH_3)(CFH_2)_2$	$O{=}P(CHF_2)_3$
$P(OCH_3)(CHF_2)_2$	$O{=}P(CHF_2)(CF_3)_2$
$P(OCF_3)(CF_3)_2$	$O{=}P(CF_3)(CHF_2)_2$
$P(OCF_3)_3$	$O{=}P(CFH_2)(CF_3)_2$
$P(CF_3)_3$	$O{=}P(CF_3)(CFH_2)_2$
$P(CH_3)(CF_3)_2$	$O{=}P(OCF_3)_3$
$P(OCHF_2)(CF_3)_2$	
$P(OCFH_2)(CF_3)_2$	

E. LOW TEMPERATURE LIMIT ESTIMATES

A major criterion for use of any compound is the ability to evaporate and fill a space to the desired concentration within the time required for extinguishment. Evaporation properties must be taken into account, specifically, evaporation equilibrium and evaporation rate.

Estimates of the ability of a compound to achieve the required air concentration under specific ambient temperature conditions can be made using the previously developed tables and figures below.

Assuming that the Troutons constants for the fluoroalkyl phosphorus compounds studied in this project are comparable to the 88 J/K-mol employed in the calculations upon which Figure 3 and Table 6 are based, yields the low temperature limit estimates listed in Table 7.

Confounding this assessment is the air reactivity of several of the compounds. Air reactivity would likely warm aerosolized droplets thus enhancing evaporation and dispersion of the chemical.

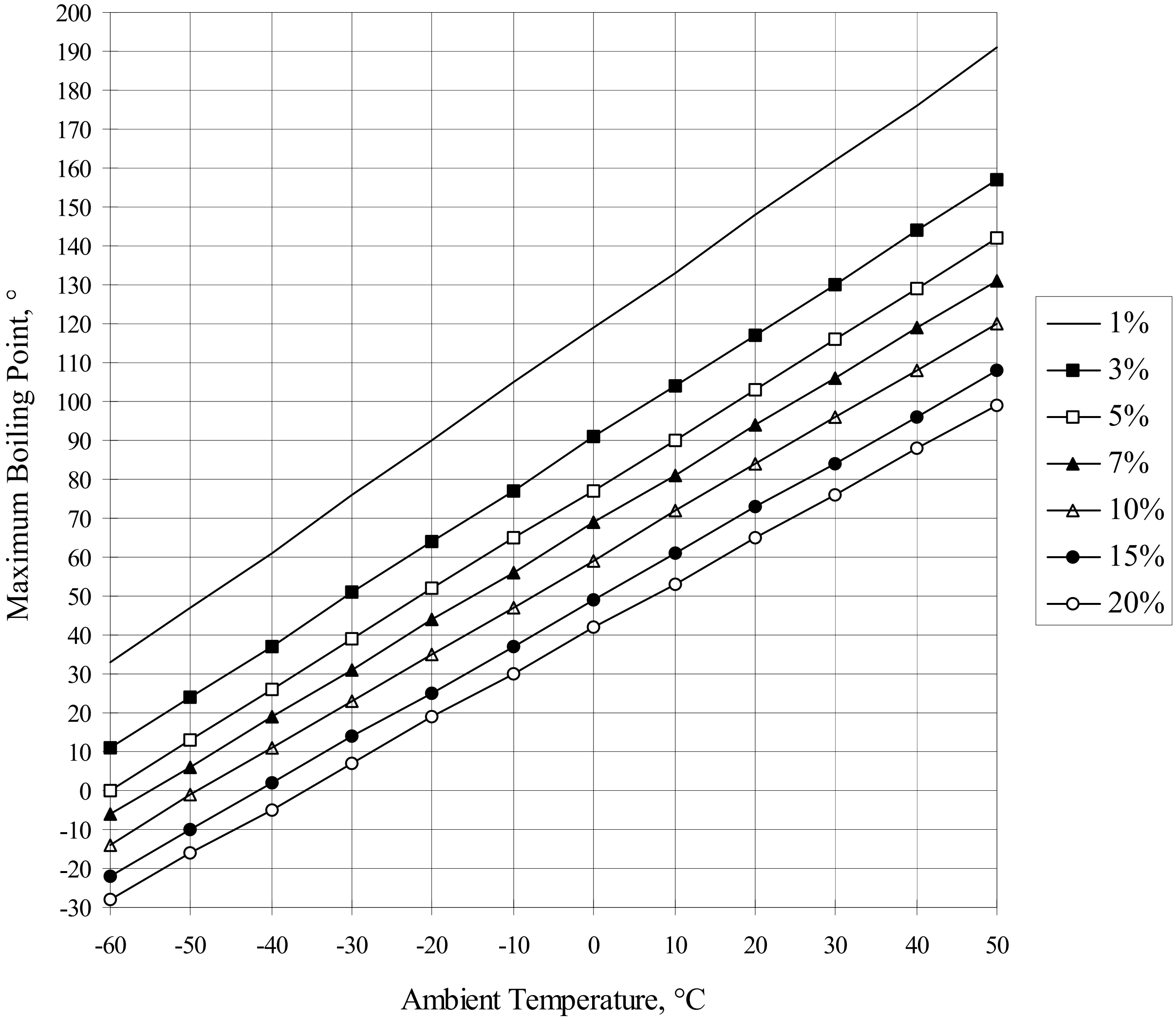

Figure 3. Estimated Maximum Boiling Points That Can Achieve Given Concentrations as Function of Ambient Temperature (Simplified), Calculated for t_c = 88 J/K-mol.

Table 6. Maximum Boiling point vs. ambient temperature and cup-burner concentration

Conc.	Ambient Temperature, °C											
%	-60	-50	-40	-30	-20	-10	0	10	20	30	40	50
1	33	47	61	76	90	105	119	133	148	162	176	191
2	19	33	46	60	74	87	101	115	128	142	156	169
3	11	24	37	51	64	77	91	104	117	130	144	157
4	5	18	31	44	57	70	83	96	109	122	135	148
5	0	13	26	39	52	65	77	90	103	116	129	142
6	-3	9	22	35	47	60	73	85	98	111	123	136
7	-6	6	19	31	44	56	69	81	94	106	119	131
8	-9	3	16	28	40	53	65	78	90	102	115	127
9	-11	1	13	25	38	50	62	74	87	99	111	124
10	-14	-1	11	23	35	47	59	72	84	96	108	120
11	-16	-3	9	21	33	45	57	69	81	93	105	117
12	-17	-5	7	19	31	43	55	67	79	91	103	115
13	-19	-7	5	17	29	41	53	65	77	88	100	112
14	-20	-9	3	15	27	39	51	63	74	86	98	110
15	-22	-10	2	14	25	37	49	61	73	84	96	108
16	-23	-11	0	12	24	36	47	59	71	83	94	106
17	-24	-13	-1	11	22	34	46	57	69	81	92	104
18	-25	-14	-2	9	21	33	44	56	68	79	91	102
19	-27	-15	-3	8	20	31	43	54	66	78	89	101
20	-28	-16	-5	7	19	30	42	53	65	76	88	99

Table 7. Temperature limits for extinguishing concentration

Compound, Formula	Boiling point, Cup-burner extinguishment %	Estimated lowest temperature at which extinguishing concentration is achievable
Bis(trifluoromethyl)methoxy phosphine, $P(OCH_3)(CF_3)_2$	55 C, NA	-38 C*
Tris(2,2,2-trifluoroethoxy) phosphite, $P(OCH_2CF_3)_3$	130 C, 3.1%	30 C
Bis(trifluoromethyl) trifluoromethoxy phosphonate, $O{=}P(OCH_3)(CF_3)_2$	42C, 4.6%	-32 C
Bis(2,2,2-trifluoroethoxy) trifluoromethyl phosphine, $P(OCH_2CF_3)_2CF_3$	111C, 3.0%	15 C
Bis(trifluoromethyl) 2,2,2-trifluoroethoxy phosphine, $P(OCH_2CF_3)(CF_3)_2$	~ 100 C, 1.8%	~ 5 C

* Assuming an extinguishment concentration equivalent to that of $P(OCH_2CF_3)(CF_3)_2$

SECTION III.
RESULTS AND CONCLUSIONS

A. RESULTS

The only non-halogen, non-transition metal elements that appear to provide any significant catalytic fire suppression capabilities are the alkali metals, tin, lead, phosphorus, and the heavier halogens (bromine, iodine, and, to a limited extent, chlorine).

B. IMPORTANT FINDINGS AND CONCLUSIONS

With one major exception, the results of the search have been disappointing as the lower boiling compound of the series tested did not demonstrate flame extinguishing properties and the lowest boiling compounds to evidence extinguishing properties were not any more effective than many of the previously studied compounds. The exception to this general conclusion is the intriguing extinguishing performance of bis(trifluoromethyl) 2,2,2-trifluoroethoxyphosphine, $P(OCH_2CF_3)(CF_3)_2$. While the compound is clearly flammable, it or its oxidation products did yield the lowest extinguishment concentration observed for the compounds tested. The structurally similar compound, bis(trifluoromethyl)methoxy phosphine, $P(OCH_3)(CF_3)_2$, may also perform well is flame extinguishment once tested. As stated previously, prior work has shown that the compound tris(2,2,2-trifluoroethyl)phosphite [25]) also exhibits a particularly low cup-burner extinguishment concentration [7] with some recent studies yielded an extinguishing concentration of 1.69 vol%. The authors have previously hypothesized that the high heat employed to vaporize the tris(2,2,2-trifluoroethyl)phosphite sample may have resulted in partial or full decomposition prior to the vapor entering the flame zone. Indeed, this project's reexamination of tris(2,2,2-trifluoroethyl)phosphite using our nebulizer based aerosolization equipment as described (see Section II.B.3), which does not subject compounds to possible thermally induced degradation yielded a cup-burner flame extinguishment value of 3.1%. These results coupled with the failure of tris(trifluoromethyl)phosphonate $O=P(CF_3)_3$ to even cause flame lift off much less flame extinguishment when tested at an air concentration of 5% seem to support a tentative conclusion that for a flame extinguishment of the fluoroalkyl phosphorus compound to be effective they must decompose readily either in the flame zone or prior to entering the flame zone.

The afore stated, tentative, conclusion may reasonably be seen as a basis to curtail interest in the further investigation of this family of compounds as halon replacements. However, incorporation of otherwise stable compounds in heat generating solid propellant gas generator devises could significantly enhance the gas generators fire suppressing effectiveness.

Few materials based on main group elements with potentially acceptable physical (primarily, volatility) and toxicological properties have been identified. The lowest molecular weight materials (i.e., the materials with the highest volatilities) often have hydrogen or halogen atoms directly attached to non-carbon atoms. The former (containing hydrogen) are often flammable, and the latter (containing halogens) are usually toxic (owing to hydrolysis). Both often have low stabilities. Moreover, few elements provide catalytic fire suppression capabilities, and compounds of most of those do not meet the requirements of this study. A major exception is fluoroalkyl phosphorus compounds, which hold significant promise despite their relatively low volatility.

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