FLUOROALKYL PHOSPHORUS COMPOUNDS
NGP ELEMENT: 4D/14/1

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ABSTRACT

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[1].

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 [2,3]. 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.

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 32 ºC [4].

This project involved the initial selection of eight promising fluoroalkyl- and hydrofluoroalkyl-substituted phosphorus compounds followed by their synthesis in the laboratory of Dr. Jean'ne Shreeve at the University of Idaho. Seven of the eight fluoroalkyl and hydrofluoroalkyl phosphorus compounds targeted for synthesis were ultimately prepared for flame extinguishment characterization using the NMERI Cup-burner.

INTRODUCTION

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[5]. Of particular interest have been compounds of phosphorus [1]. Phosphorus compounds appear to provide a chemical fire extinguishment mechanism, and some appear to be highly effective [6].

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. These groups have the potentially of lower boiling points and reduction in the presence of hydrogen atoms contributes to a reduction in flammability. For example, tris(2,2,2-trifluoroethyl)phosphite ($P(OCH_2CF_3)_3$, TFEP) had 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)phosphate, has been reported to have a normal boiling point of 32 C. The hypothetical compound $P(OCF_3)_3$, tris(trifluoromethyl)phosphite should also have significant volatility as its reported boiling point is 32º C.

Several phosphorus compounds representing alkyl 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 nonflammablity 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.

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. Selected Target Compounds

#	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) Phosphine	$P(OCH_2CF_3)_3$
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.
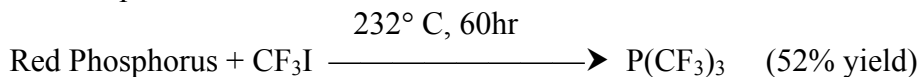
SYNTHETIC APPROACH

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.
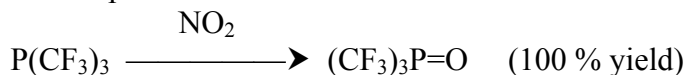
Synthesis 1:

This two step synthesis involved reaction of red phosphorus with CF_3I forming the flammable intermediate (CF3)3P followed by an oxidation insertion reaction with nitrous oxide and nitrogen dioxide to form the phosphonate, $(CF_3)_3P=O$[8].

Step 1.

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

Step 2.

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

Synthesis 2:

The $(CF_3)_2PI$ formed as one of the products in 25% yield from the reaction of CF_3I and red phosphorus was reacted at 25 ˚C with AgCl to form $(CF_3)_2PCl$ in ~100% yield. The chloride was subsequently reacted with methanol in the presence of triethyl amine [9].

$$(CF_3)_2PCl \xrightarrow[\substack{(CF_3CH_2)_3N}]{CH_3OH} (CF_3)_2POCH_3 \quad (85\% \text{ yield})$$
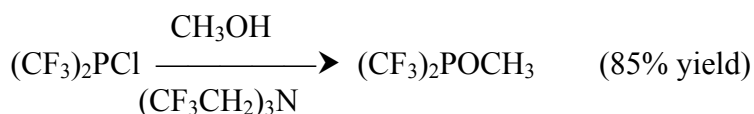
Synthesis 3:

The synthesis of $P(OCH_2CF_3)_3$ was carried out by adding trifluoroethanol dropwise into a vigorously stirring solution of phosphorus trichloride (slight excess) at 0˚C. After five hours, fractional distillation gave the desired product.
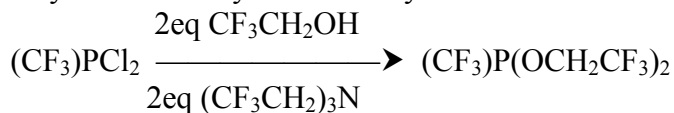
$$PCl_3 + CF_3CH_2OH \longrightarrow P(OCH_2CF_3)_3 \quad (100\% \text{ yield})$$

Synthesis 4:

The $(CF_3)_2POCH_3$ was oxidized with a slight molar deficiency of nitrogen dioxide as in Synthesis l. The NO was removed under vacuum.
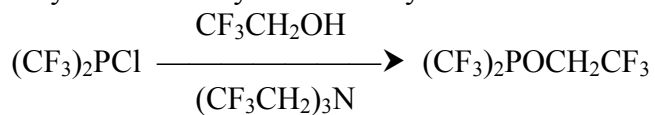
$$(CF_3)_2POCH_3 \xrightarrow{NO_2} (CF_3)_2P(O)OCH_3 \quad (100\% \text{ yield})$$
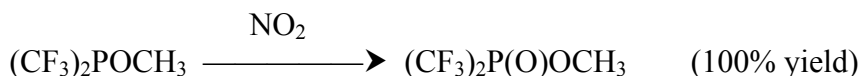
Synthesis 5:

This synthesis is very similar to Synthesis 2 above.

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

Synthesis 6:
This synthesis is very similar to Synthesis 2 above.

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

Synthesis 7:
This synthesis is very similar to Synthesis 4 above.

$$(CF_3)_2POCH_2CF_3 \xrightarrow{NO_2} (CF_3)_2P(O)OCH_2CF_3$$
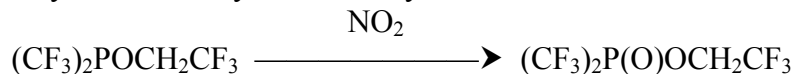
Synthesis 8:
This synthesis attempt was unsuccessful but very similar to Synthesis 1 in execution.

$$(CF_3)_3P \xrightarrow{O_2} (CF_3O)_3P{=}O \quad \text{(reaction failed to yield isolable product)}$$
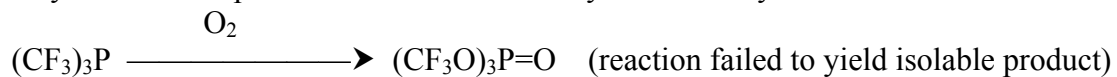
The synthetic products of the above reaction are summarized in Table 2. Final product weights and boiling points are listed.

Table 2. Compound Synthesis Status and Boiling Points

| #	Compound - Formula	Boiling Point ºC	Synthetic product weight (g)
1	Tris(trifluoromethyl) Phosphonate $O=P(CF_3)_3$	32º C	7.3
2	Bis(trifluoromethyl)methoxy Phosphine, $P(OCH_3)(CF_3)_2$	55º C	5.3
3	Tris(2,2,2-trifluoroethoxy) Phosphine, $P(OCH_2CF_3)_3$	130º C @ 743 mm	50.0
4	Bis(trifluoromethyl) trifluoromethoxy Phosphonate, $O=P(OCH_3)(CF_3)_2$	42º C @ 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, $P(OCH_2CF_3)(CF_3)_2$	25º C @ 50mm	6.5
7	Bis(trifluoromethyl) 2,2,2-trifluoroethoxy Phosphonate, $O=P(OCH2CF_3)(CF_3)_2$	130º C (estimate)	7.0
8	Tris(trifluoromethoxy) Phosphonate, $O=P(OCF_3)_3$	32º C	Not synthesized

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 to be 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. 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.
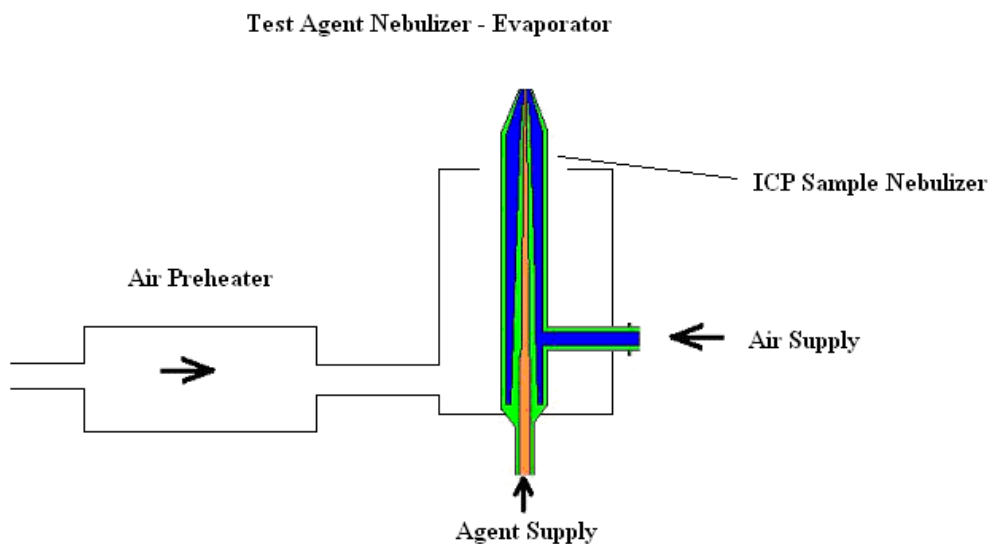
The nebulizer employed in this apparatus is a standard feature in all atomic emission inductively coupled spectrometers. These devices readily aspirate samples at rates of 1 to 3 cc's per minute at air pressures of ~40psig. They can also be forced to higher levels of output by employing a syringe pump 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 3hp compressor. Air flows were set and monitored using a mass flow meter.
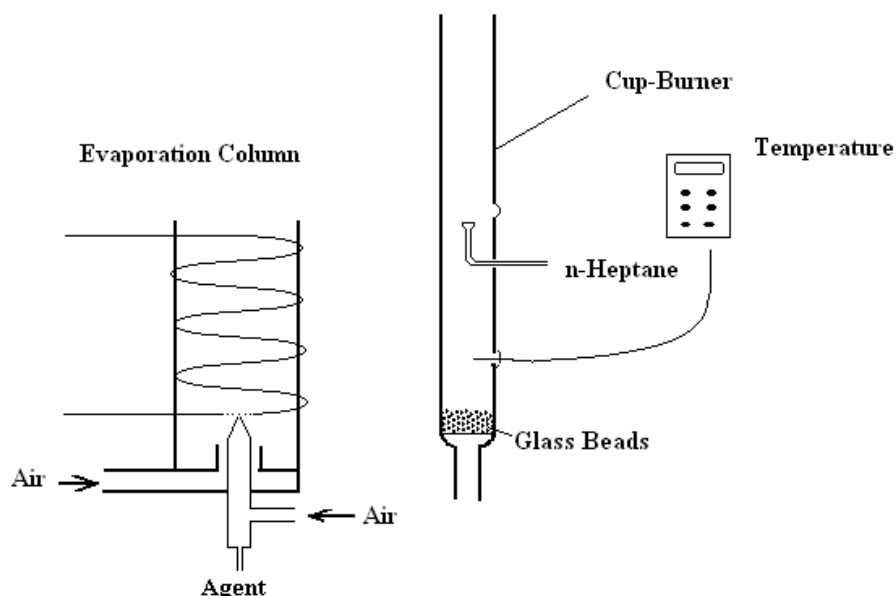
Figure 2. Cup-burner equipped with sample nebulizer and evaporation column

Table 3. Summary of Cup-Burner Results

#	Compound, Formula	Cup-burner Testing
1	Tris(trifluoromethyl) Phosphonate, $O=P(CF_3)_3$	No extinguishment 5%
2	Bis(trifluoromethyl)methoxy Phosphine, $P(OCH_3)(CF_3)_2$	Spontaneously ignites w/air *
3	Tris(2,2,2-trifluoroethoxy) Phosphine, $P(OCH_2CF_3)_3$	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, $O=P(OCH2CF_3)(CF_3)_2$	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 $O=P(OCH_2CF_3)(CF_3)_2$ or a undergoes oxygen insertion reactions of the P-CF3 bonds. Air reactivity observations are summarized in Table 4.

Table 4. Air Stability Observations

#	Compound - Formula	Observation
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) Phosphine, $P(OCH_2CF_3)_3$	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

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 efficient fire suppression, 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). Phosphenes 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. Phosphines (compounds 2, 3, 5, and 6) 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 (>250º 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.

RECOMMENDATIONS

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 base suppressants for aircraft applications;
- The break down products of compounds 2 and 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 42º C boiling point) border on acceptability for aircraft applications. Additional effort directed to the

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acquisition of fluoro-phosphorus compounds similar to $P(OCH_3)(CF_3)_2$ with -$OCFH_2$ instead of -OCH_3 is indicated;

- The synthesis attempted of compound 8 had been reported in the literature. While the recent synthesis effort was unsuccessful, a realistic expectation of its acquisition still exists. The 32º C boiling point of compound 8 as well as its similarity to the structures thought to be the breakdown products from compound 6, that are thought to possibly result in 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.

ACKNOWLEDGMENTS

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