

PROJECT REVIEWS: TROPODEGRADABLE BROMOCARBON EXTINGUISHANTS – II AND FLUOROALKYL PHOSPHORUS COMPOUNDS

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INTRODUCTION

In two projects sponsored by the Department of Defense Next-Generation Fire Suppression Technology Program (NGP), research efforts at The University of New Mexico are evaluating chemical agents as substitutes for Halon 1301[1]. The first of these, a project titled “Tropodegradable Bromocarbon Extinguishants-II,” is approximately half way through its planned effort. The second project is entitled “Fluoroalkyl Phosphorus Compounds.” This project targets the acquisition and testing of promising fluoroalkyl phosphorus compounds and has just received funding. This report summarizes the efforts undertaken or to be undertaken in each of these projects and the progress and achievements to date.

‘TROPODEGRADABLE BROMOCARBON EXTINGUISHANTS – II

This effort is a continuation of an earlier successful NGP project, which resulted in the acquisition of several tropodegradable compounds with very promising cup-burner flame extinguishment properties. Several of these bromofluoroalkenes were evaluated in acute inhalation toxicity tests [1, 2], Ames mutagenicity studies,* and *In Vitro* Chromosome Aberration Tests using human peripheral blood lymphocytes.* Cardiac sensitization testing is planned for the most promising compound, 2-bromo-3,3,3-trifluoropropene. Testing results to date are very favorable, and there is strong indication that as a group the tropodegradable bromocarbons may well yield acceptable replacements for Halon 1301.

Based on an analysis of atmospheric reactivity, various chemical families are recognized as having the potential to be tropodegradable or capable of essentially complete decomposition within the troposphere and therefore not posing a threat to stratospheric ozone. The tropodegradable chemical families, initially of interest for development of tropodegradable bromocarbon extinguishants, are listed below.

- Brominated Alkenes
- Brominated Alkyl amines
- Brominated Aromatics
- Brominated Ethers
- Brominated Alcohols
- Brominated Carboxylates

Of these chemical families the brominated alkenes, ethers, and amines were judged the most likely to meet desired boiling point restrictions, environmental, and toxicity goals; of these families the bromofluoroalkenes were judged the most favorable based on atmospheric lifetime. Toxicity requirements are generally viewed as presenting the most difficult hurdle in the development of halon replacements.

Early research work on new total-flood agents established the potential of tropodegradable bromocarbons as fire suppressants; however, flame extinguishment experiments were insufficient to relate performance (and, for some compounds) flammability to structure [2-6]. NMERI's recent NGP project was conceived in part to address the need for more laboratory-scale fire extinguishment information on tropodegradable compounds. The first project on tropodegradable compounds funded under the NGP program identified several bromofluoroalkenes and bromofluoroamines with good flame extinguishment performance. No bromofluoroethers were acquired or synthesized during this first effort due to funding and time constraints as well as synthesis and sourcing difficulties.

This report summarizes the current acquisition and extinguishment studies on tropodegradable bromocarbon extinguishants. These studies are adding to the number of characterized compounds and identify-

* Reports available from the **Advanced** Agent Working Group.

ing compounds with significantly lower boiling point. In addition, new screening techniques have been developed for performing ISO as well as NMERI cup-burner testing of small quantities of compound.

EARLY DEVELOPMENT EFFORTS

Commercialized halon replacements such as perfluorocarbons (PFC, FC), hydrochlorofluorocarbons (HCFC), hydrofluorocarbons (HFC), hydrofluoropolyethers (HFPE), and iodofluorocarbons (CF₃I) do not contain bromine and therefore are not as effective in flame extinguishment tests or actual large-scale fire suppression tests due for the most part to the absence of bromine in the structures of these chemicals.

Low atmospheric lifetime compounds provide an opportunity to retain bromine in the extinguishant molecule. Alkenes, for instance, which readily react with atmospheric •OH and O₃ can act as a carrier (Table 1). The resulting brominated compound will still rapidly degrade in the troposphere and never reach the stratosphere or the earth's ozone layer.

TABLE 1. TROPODEGRADABLE CARRIERS AND BROMINATED DERIVATIVES

Tropodegradable Base Structure	Tropodegradable Bromocarbon Derivative
CH ₂ =CHCF ₃	CH ₂ =CBrCF ₃ , CHBr=CHCF ₃
CH ₂ =CF ₂ CF ₃	CHBr=CF ₂ CF ₃
CH ₂ =CF ₂ CF ₂ H	CH ₂ =CHCF ₂ Br, CHBr=CF ₂ CF ₂ H
CHF=CHCF ₃	CBr=CHCF ₃ , CHF=CBrCF ₃

When bromine is contained within the molecular structure of a short atmospheric lifetime compound, the resulting chemical is referred to a tropodegradable bromocarbon. All the carrier compounds would only be partially fluorinated. Other incorporated chemical features reactive with atmospheric •OH or O₃ are found in partially fluorinated amines, ethers, and alcohols. Iodinated compounds such as CF₃I are short atmospheric lifetime tropodegradable compounds due to the rapid photolysis of the C-I bond, which results from exposure to sunlight.

Although tropodegradable compound atmospheric lifetimes have been measured, they are generally estimated based on data generated for functional groups such as sites of unsaturation, numbers of C-H bonds, and substitution patterns. For alkenes, atmospheric lifetimes as low as a few days have now been experimentally determined.* Amines are estimated to have atmospheric lifetimes on the order of one or more months. Ethers are estimated to have atmospheric lifetimes of days to months. The brominated ether CH₃OCF₂CHBr (commonly known as Rofluorane) has been reported to have an atmospheric lifetime of 14 days [7].

The reactions that cause atmospheric decomposition of a molecule differ for alkenes, ethers, and amines. For alkenes, reactions with hydroxyl free radicals or with tropospheric or ground level ozone are expected to target the double bond while ethers and amines would be subject to hydrogen abstraction reactions by the •OH radical. As stated above, photolysis of the C-I bond is the predominant reaction pathway for iodinated fluoroalkanes such as CF₃I.

The problem is one of selecting appropriate toxicity end points and developing a ranking of their relative importance. This information became part of the basis for the preliminary screening prior to actual acquisition and or synthesis efforts. An example of the selection criteria developed early in the Halon 1301 replacement program is presented in Table 2.

* Vladimir Orkin, NIST, personal communication, April 2000.

TABLE 2. HALON 1301 REPLACEMENT CANDIDATE CRITERIA.

Criteria	Value
Boiling point	< ~ 50 °C
LC ₅₀ ^a (4-hour)	> 50,000 ppm (5.0%)
Cup-burner performance	< 5.0%
ODP	<0.02
GWP	< 5,000
Atmospheric lifetime	Days to months
Cardiac sensitization (CS _{NOAEL})	> 2 times cup-burner performance

^aLowest concentration causing death in 50% of an animal test population.

The initial selection criteria listed in Table 1 do not do justice to the challenges facing halon replacement research. Some of the major hurdles, yet to be addressed, are listed below. Prominent among these are manufacturability and end-user cost. To have the greatest likelihood of success, the program must identify as many functionally and environmentally acceptable compounds as is practical. This is one reason why continued compound acquisition efforts are essential.

- Other toxicity and exposure criteria
- Chemical Stability
- Manufacturability (production cost)
- Materials Compatibility

Functional upper limits for the boiling points of compounds for total-flood agent applications are presented in Table 3. Estimates of theoretical ambient vapor pressure as a function of boiling point and ambient temperature (based on Trouton's constant) are shown, but of course they say nothing about the time required to establish the targeted air concentration. In the case of total-flood agents, vapor pressure under the conditions of usage are seen as a primary factor in the fire or explosion performance of an agent. This table has been presented elsewhere and is shown here in a modified form to illustrate the problems associated with developing agents for low temperature applications and the significance of identifying compounds with lower boiling points and cup-burner values. The shaded area of the chart reflects the lowest boiling points of the compounds acquired and tested in our previous project. From the chart it can be seen that to achieve an additional -10 °C lower application temperature the upper limit on agent boiling point must be reduced by 13 °C. Similarly, dropping the cup-burner based required extinguishant air concentration by 1% is equivalent to allowing compounds with 6-8 °C higher boiling points to be considered. If both a 10 °C lower boiling point and a 1% lower cup-burner effect are combined, the "Ambient Temperature" application limit is decreased approximately 15 °C.

TABLE 3. ESTIMATES OF MAXIMUM USABLE BOILING POINTS.

Air Concentration (%)	Ambient Temperature, °C								
	-60	-50	-40	-30	-20	-10	0	10	20
1	33	47	61	76	90	105	119	133	148
2	19	33	46	60	74	87	101	115	128
3	11	24	37	51	64	77	91	104	117
4	5	18	31	44	57	70	83	96	109
5	0	13	26	39	52	65	77	90	103
10	-14	-1	11	23	35	47	89	72	84
15	-22	-10	2	14	25	37	49	61	73

Example. To achieve a 4 vol % concentration at -20 °C, the maximum allowable boiling point is 87 °C

CURRENT PROJECT EFFORTS

The list of bromofluoroalkenes acquired prior to the start of the current project are listed in Table 4. The data all indicate that regardless of compound structure, straight chain or branched, and propene, butene, or pentene derivative, the flame extinguishment is generally below 4% with most of the tested compounds

TABLE 4. BROMINATED TROPODEGRADABLE HALOCARBON CUP-BURNER VALUES.

Compound	Formula	Boiling Pt, °C	Cup Burner, %
1-Bromo-3,3,3-trifluoropropene	CF ₃ CH=CHBr	40	3.5*
3-Bromo-3,3-difluoropropene	CBrF ₂ CH=CH ₂	42	4.5
2-Bromo-3,3,3-trifluoropropene	CF ₃ CBr=CH ₂	34	2.6
4-Bromo-3,3,4,4-tetrafluorobutene	CF ₂ BrCF ₂ CH=CH ₂	54	3.5
2-Bromo-3,3,4,4,4-pentafluorobutene	CF ₃ CF ₂ CBr=CH ₂	56	3.8*
2-Bromo-3,3,4,4,5,5,5-heptafluoropentene	CF ₃ CF ₂ CF ₂ CBr=CH ₂	78	3.7*
2-Bromo-3-trifluoromethyl-3,4,4,4-tetrafluorobutene	CF ₃ CF(CF ₃)CBr=CH ₂	78	3.3*
2-Bromo-3-trifluoromethoxy-3,4,4,4-tetrafluorobutene	CF ₃ CF(OCF ₃)CBr=CH ₂	75	3.8*
1-Bromo-2-trifluoromethyl-3,3,3-trifluoropropene	(CF ₃) ₂ C=CHBr	63	2.6*
1-Bromo-4,4,4,3,3-pentafluorobutene	CF ₃ CF ₂ CH=CHBr	58	3.1*

* Testing performed using premixed agent/air mixtures

yielding NMERI cup-burner values comparable to Halon 1301. Only when the degree of fluorination falls to less than 50% of available positions (total of number of Hs, fluorines, and bromines) does the cup-burner value rise significantly above 4%.

The current project seeks to identify and acquire highly effective flame extinguishments compounds with boiling points significantly below 34 °C. Those compounds acquired thus far are listed in Table 5. Data for those whose extinguishments have been tested in the NMERI cup-burner are indicated. Boiling points for several of the acquired compounds are as much as 9 °C lower than observed earlier. Additional compounds are now being selected for acquisition.

TABLE 5. SUMMARY OF NEW COMPOUNDS ACQUIRED.

Compound	Formula	Boiling Pt, °C	Cup Burner, %
1-Bromopentafluoropropene	CFBr=CFCF ₃	27 - 28	----
2-Bromopentafluoropropene	CF ₂ =CBrCF ₃	25 - 26	(3.5)
2-Bromo-1,3,3,3-tetrafluoro-1-propene	CFH=CBrCF ₃	29 - 32	(3.7)
3-Bromo-1,1,3,3-tetrafluoro-1-propene	CF ₂ =CHCF ₂ Br	33	(3.3)
1-Bromo-1,3,3,3-tetrafluoro-1-propene	CFBr=CHCF ₃	----	----
Bromomethyl trifluoromethyl ether	CH ₂ Br-O-CF ₃	39 - 41	3.2
Bromomethyl difluoromethyl ether	CH ₂ Br-O-CF ₂ H	70	----
Bromoethyl trifluoromethyl ether	CBrH ₂ CH ₂ -O-CF ₃	----	----

* Testing performed using premixed agent/air mixtures (V/V); () indicates preliminary data.

To determine the cup-burner flame extinguishments, NMERI developed a reliable method for preparing air/agent mixtures that requires as little as 2 g of test compound (Figure 1). This enables the study of compounds that can be acquired only from sources of custom synthesis at a cost that in general would prohibit the acquisition of the large amounts of test material typically required (50–200 g). The method

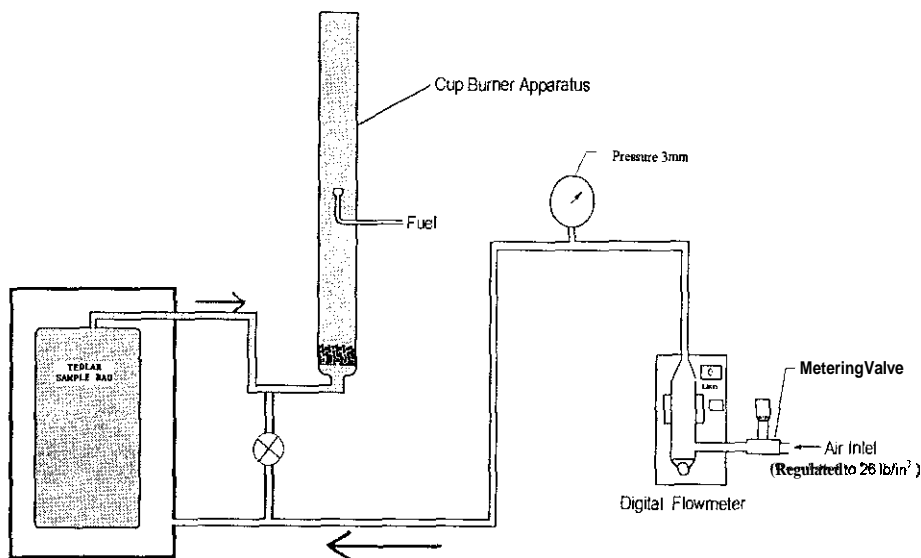


Figure I. NMERI cup-burner agent/air sample flow diagram

TABLE 6. COMPARISON OF ISO AND NMERI CUP-BURNERS.

Air Concentration, % (V/V)	n-Heptane Flame Extinguishment		
	ISO Burner: (20L/min)	(30L/min)	NMERI Burner: (10L/min)
3.6	Yes	Yes	Yes
3.2	Yes	Yes	Yes
3.1	Yes	No	Yes
3.0	Yes	No	Yes
2.8	No	---	No

as first developed employed the 10L Tedlar™ air sampling bag typically used in environmental or Industrial hygiene monitoring. The Tedlar™ bag itself is contained within a rigid walled airtight outer container. Air, at the flow rate being employed in the cup-burner test, is directed into the region between the rigid container and Tedlar™ bag resulting in discharge of the air/agent mixture from the Tedlar™ sample bag into the base of the cup burner. The method allows for serial dilution of the air agent mixture and sequential extinguishment tests at ever decreasing agent/air concentrations. The method has now been extended to 100L Tedlar™ sample bags. This has allowed the side-by-side comparison of NMERI and ISO cup burners using the same air/agent sample. Flame extinguishment data from this comparison (Table 6) demonstrate the relative similarity of NMERI and ISO cup-burner data for gaseous agents. This study is being extended to liquid agents such as those being acquired in this project.

CONCLUSION

As presented in this review, tropodegradable bromofluoroalkenes have been demonstrated to be effective fire extinguishants in both streaming and total flood applications. Cup-burner data indicate that for compounds where the degree of fluorination is equal to or greater than 50% the extinguishment concentrations are as low as 2.6%. Boiling points for many of the compounds acquired now range from a low of 25 to 74 °C. Actual testing of the performance of these compounds in fire and explosion suppression tests at sub-ambient temperature conditions is needed to assess performance and evaluate the significance of dispersion and droplet size effects on extinguishment. Toxicity testing results for the bromofluoroalkenes continue to be very promising, and further testing is planned in the near future.

Overall, the compound search has had very positive results. Bromofluoroalkenes as a class have exhibited considerable promise as potential halon replacements. Further acquisition of compounds related to **2-bromo-3,3,3-trifluoropropene** and **4-bromo-3,3,4,4-tetrafluorobutene** will likely lead to the identification of additional low boiling candidates. Continued acquisition and testing programs will also include studies of bromofluoroethers and, to a lesser extent, bromofluoroamines as these two classes of compounds have shown promise in the limited testing performed.

- Develop new lists of bromofluoroalkenes and bromofluoroethers for acquisition and testing with the continued focus being on low boiling compounds.
- Perform additional flame extinguishments studies comparing the performance of ISO and NMER1 cup burners.

FLUOROALKYL PHOSPHORUS COMPOUNDS

On 11 April, the project Fluoroalkylphosphorus Compounds was awarded under the Next-Generation Fire Suppression Technology Program (Project 4D/14/1). The primary objective of the project, which is scheduled to run from 11 April 2001 through 10 April 2002, is the synthesis and extinguishant testing of low molecular weight fluoroalkylphosphorus compounds.

OVERVIEW

Phosphorus compounds show extraordinary effectiveness as flame extinguishants, and there is evidence for a chemical mechanism [8]. 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. A well-studied example is dimethyl methyl phosphonate [(O)P(OCH₃)₂CH₃], which exhibits good fire suppression, but which is flammable and has a very low volatility [9,10]. Phosphorus compounds containing fluoroalkyl and hydrofluoroalkyl groups are often nonflammable and have higher volatilities than the non-fluorinated analogs. At the Halon Options Technical Working Conference (HOTWC 2000), the Defense Evaluation and Research Agency reported extinguishing concentrations for a number of partially fluorinated phosphates [11]. Owing to their high molecular weights, however, these compounds still had a very low volatility.

This project targets the identification, synthesis, and laboratory testing of fluoroalkyl- and hydrofluoroalkyl-containing phosphorus compounds as fire extinguishants, with an emphasis on low molecular weight compounds. These materials are expected to be more volatile and effective than the corresponding non-fluorinated compounds and more volatile than the higher molecular weight fluorinated compounds studied in the past. The following will be accomplished: (1) lower molecular weight phosphates, phosphites, phosphonates, and related compounds containing fluoroalkyl and hydrofluoroalkyl groups that have potential to be synthesized and are expected to perform well as fire extinguishants will be identified; (2) under a subcontract to The University of New Mexico, Prof. Shreeve (University of Idaho) will prepare the compounds identified in Task 1; and (3) cup-burner and physical property determinations will be performed.

COMPOUNDS SELECTED

Although this project has only very recently been initiated, a preliminary list of compounds to be targeted has been developed (Table 7). This list is still subject to modification.

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TABLE 7. SELECTED COMPOUNDS.

Compound	Boiling Point
O=P(CF ₃)	32 °C
P(OCF ₃) ₃	
O=P(OCH ₃)(CF ₃) ₂	42 °C (745 mm)
P(OCH ₃)(CF ₃) ₂	55 °C
O=P(OCF ₃) ₃	51 °C
O=P(OCH ₂ CF ₃)(CF ₃) ₂	
P(OCH ₂ CF ₃)(CF ₃) ₂	
P(OCH ₂ CF ₃) ₃	130-131 °C (743 mm)
P(OCH ₂ CF ₃) ₂ CF ₃	110-112 °C

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