

OLEFINIC CHLOROFLUOROCARBON (OCFC) FIRE EXTINGUISHING AGENTS

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ABSTRACT

A new concept has been devised for volatile olefinic chlorofluorocarbon (OCFC) agents that may have the fire extinguishing capabilities of conventional halons, and that could be derived by pyrolysis of non-volatile precursors (NVPs) upon exposure to heat in fire zones. Such NVP/OCFC agents would have no ozone depletion, global warming, or toxic vapor problems. Several types of NVPs are being considered, including compounds capable of emulsification in aqueous film forming foam (AFFF) formulations, fire retardant intumescent paints, resins, and water soluble polyether or similar types of compounds. Several OCFC agents are being prepared and tested for fire extinguishing capabilities by the University of Lowell / Center for Global Environmental Technologies team. The first to be tested, 4-bromo-3-chloro-3,4,4-trifluoro-1-butene has proven to be quite effective. Thus, a 5% concentration of this OCFC extinguished fires in cup-burner tests, as compared with values of 4% for Halon 1211 and 6% for HCFC-123, the latter being of great current interest as a Halon alternative. In view of the highly encouraging results of this first effort, several other OCFC agents are being tested in this phase of research. The most promising OCFC groups will be incorporated into larger molecules that when exposed to flames, will pyrolyze to free the OCFC agent. The functional groups into which the OCFC precursors will be incorporated include carboxylate ester, carboxylamide, ammonium cation, amine oxide, and similar functionalities which can be pyrolyzed to generate the OCFCs.

NON-VOLATILE PRECURSORS  
TO OLEFINIC CHLOROFLUOROCARBONS (NVP/OCFCs)  
AS ALTERNATIVE FIRE EXTINGUISHING AGENTS  
WITH REDUCED GLOBAL ENVIRONMENTAL IMPACTS.

PHASE I. SYNTHESIS AND STUDY OF OCFC CANDIDATES.

INTRODUCTION

Responsible scientific organizations have determined that industrially produced chlorofluorocarbon (CFC) emissions pose serious environmental and health problems in terms of unacceptably high stratospheric ozone depletion potentials (ODPs). This ozone layer has been well demonstrated to be necessary for protection of life on earth from damaging ultraviolet radiation. CFCs are used as refrigerants, foam-blowing agents for polymeric formulations, industrial solvents, and aerosol propellants. The very efficient Halon fire extinguishing agents (principally Halon 1211 and Halon 1301) are bromofluorocarbons (BFCs), chemically related to CFCs; these also pose serious threats to stratospheric ozone. Both CFCs and BFCs have also been demonstrated to pose unacceptably high global warming potentials (GWP). Throughout the rest of this discussion the term "CFC" will pertain to both CFC and BFC types of agents.

Most emission problems are due to leaks and spills of gaseous CFCs from the refrigerators and air conditioners.

Recently, however, there have been significant increases in atmospheric concentrations of Halon 1211 arising from releases resulting from fire fighting, firefighter training, system testing, and accidental discharges and leakages. It is estimated that Halons account for 15% of the total ODP problem. Regulatory commissions such as the EPA have called for cooperative efforts to stem the rate of emissions and to seek effective alternative firefighting agents.<sup>1,2,3,4,5</sup>

In a definitive study of criteria for "Next-Generation Fire Extinguishing Agents", Dr. Robert Tapscott of the New Mexico Engineering Research Institute (NMERI) has identified some problems with existing Halons, in addition to the environmental ozone problems, which apply to currently used Halon fire extinguishing agents:<sup>6</sup>

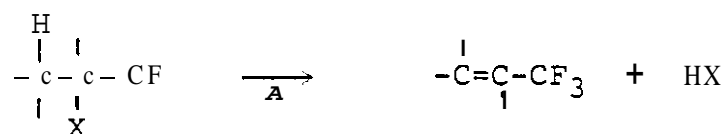
1. Halon agents in current use (especially Halons 1211 and 2402) have high enough toxicities to cause human deaths.
2. The gaseous Halons currently in use have poor deliverability in outdoor situations.
3. Gaseous Halons which are now used do not provide good security (*i.e.*, these dissipate rapidly) when applied to burning liquids.

In addition, it was postulated that olefinic Halon agents (though not yet available in bulk) could serve as superior extinguishing agents.

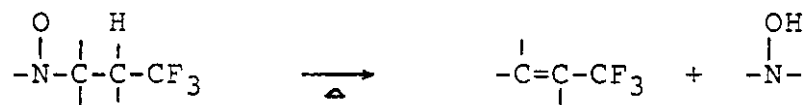
A variety of well-developed synthetic approaches exist for the preparation of olefinic compounds. These approaches include thermal degradations of alkyl halides, amine oxides, substituted ammonium halides, alcohols, esters, and other organic functional groups, as shown in Table I.<sup>7</sup>

TABLE I. THERMAL DEGRADATION SCHEMES<sup>7</sup>

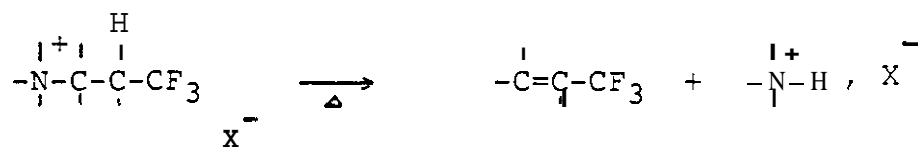
a. Dehydrohalogenation of haloalkanes



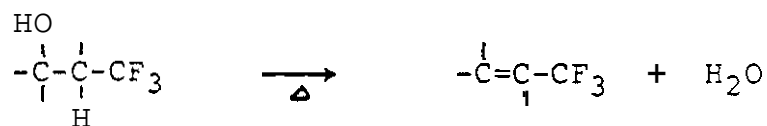
b. Amine oxide eliminations ("Cope")



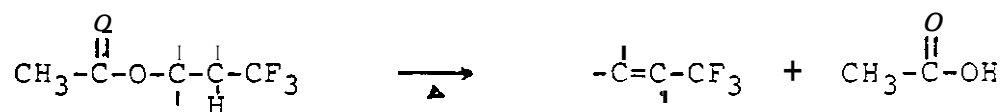
c. Ammonium halide eliminations ("Hofmann")



d. Dehydration of alcohols



e. Ester pyrolysis ("Bailey")



Therefore, the ultimate goal of future phases of this research will be to synthesize, test and evaluate a series of olefinic halon precursors. These precursors would be capable of generating olefinic halons by thermal decomposition specifically and only in zones heated by contiguous or prior flame activity. In this way, the volatile halon that would function as the actual extinguishing agent would be produced only when and where needed, by pyrolytic decomposition of higher molecular weight non-volatile precursors (NVPs).

It is of interest to note that surfactants such as those in AFFF formulations may have unique capabilities for enhancing rates of thermal decompositions of NVP/OCFC agents to form these OCFCs. Thus, as will be discussed later, the NVP could be an additive which could be emulsified by the AFFF surfactant; or the NVP could be incorporated into the surfactant molecule itself. Surfactants exist in water as micelles, which are clusters of many surfactant molecules in small globules in the water to which the agent is added. These micellar structures can emulsify and carry other organic materials into an emulsion with water. The ionic or polar "head" groups of the molecules of the emulsified micellar aggregates are arranged at the interface of the micelle with the surrounding water, with the hydrophobic hydrocarbon "tails" of the surfactant molecules pointing into the micelle. Thus, even though the system is literally drenched in water, the interiors of the micellar structures

(along with any materials carried into the interiors of the emulsified micelles) are totally dry.<sup>8,9,10</sup> (See Figure 1.)

Figure 1. Micellar emulsification of NV? materials in AFFF.

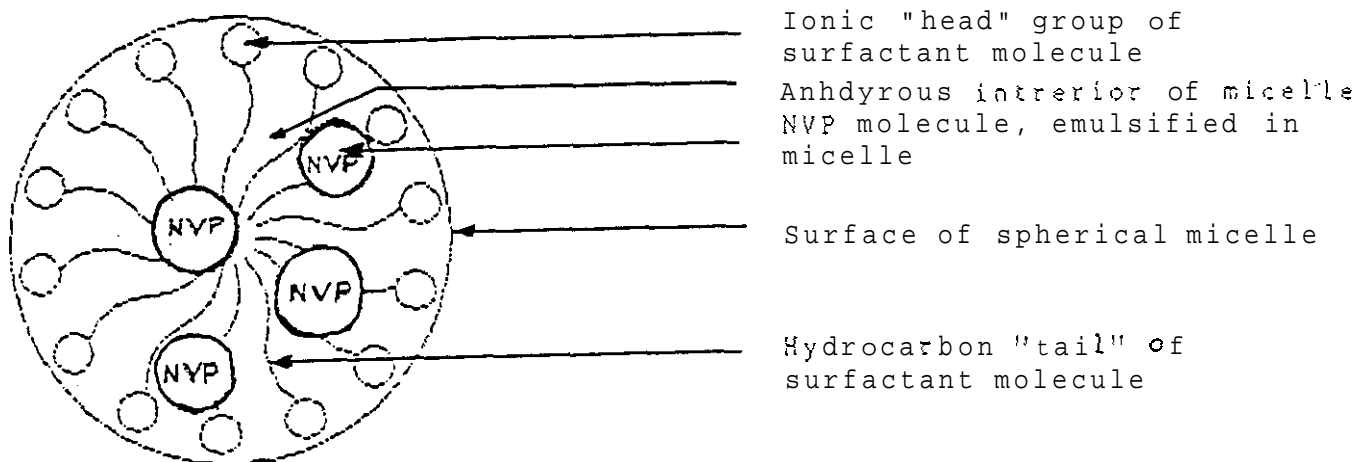
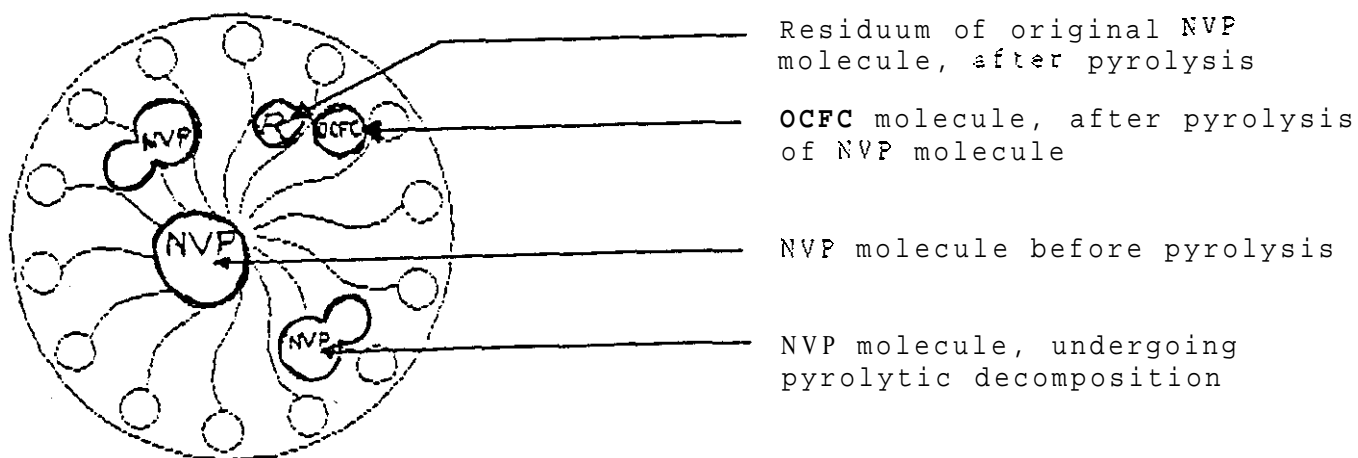


Figure 2. Micelle catalyzed pyrolysis of emulsified NV? molecules



It has previously been demonstrated by members of this group<sup>11</sup> and by others<sup>12-17</sup> that, on the one hand, water tends to stabilize reactants such as are contained in Table I, which can be pyrolyzed to form olefinic decomposition products. On the other hand, very importantly, when

molecules with these groups are emulsified into the anhydrous interiors of surfactant micelles, the decomposition rates are greatly increased. Thus, a feasibility may exist to develop NVP/OCFC formulations which could be stored for long periods of time without decomposition, either in water solution or suspension. When added to an AFFF agent and emulsified in water, these agents would very quickly and easily decompose to form an olefinic chlorofluorocarbon (OCFC) extinguishing agent when applied to a hot fire zone in an AFFF hose stream.

Since no agent would be lost by evaporation along its trajectory into the fire zone, the amount of agent required for effective firefighting would be drastically reduced. Also, only that portion **of** the delivered agent which actually contacts the hot fire zone would emit volatile Halon; this would further serve to reduce Halon emissions very significantly, with concomitant increases in agent security. In addition, because acute toxicity effects of volatile agents are much more severe than effects of nonvolatile materials, the toxicity problems posed by exposure of firefighters to these agents would be greatly reduced.

These Halon precursor agents, and their olefinic Halon pyrolysis products, are as "clean" as AFFF formulations. Thus, no residual ash will result upon exposure to heat or combustion processes. At least some of the precursor agents (e.g., quaternary ammonium salts) might be anticipated to

show anti'-corrosionactivity for exposed metal surfaces which these agents may contact.<sup>18</sup>

The proposed Halon precursor agents could also be formulated as paints, resins or other coating materials for use in safes, computers, munition storage areas, waste baskets, and in similar areas in which a desirability would exist for thermally induced release of volatile halons.

In all these applications, there would be no emissions of Halon to the atmosphere as a result of tank leakages, inadvertent valve openings, and similar sources of accidental releases that currently pose enormous environmental problems.

#### RESEARCH PROTOCOL

For the initial phase of the research, the following phases of RDT&E efforts were proposed:

A. Synthesis of volatile olefinic halons.

The fire extinguishing capability of the volatile olefinic Halon formed in each of these cases would be crucially important to the feasibility of the system. Therefore, the first phase of the proposed project involves the synthesis, testing, and evaluation of prototype olefinic halon fire extinguishing agents which could be produced by pyrolysis of the chemical families indicated above.



Candidate olefinic Halons include those listed in Table 11, to be prepared using techniques described in the literature as indicated, with subsequent cup burner tests (as have been developed and tested at NMERI)<sup>4</sup> to be performed to evaluate the extent of halon extinguishing capabilities.

TABLE 11. CANDIDATE OCFC AGENTS TO BE SYNTHESIZED

	Reference
$\text{BrCH}=\text{CBr}-\text{CF}_3$	20
$\text{BrCF}=\text{CF}-\text{CF}_3$	21
$\text{CF}_2=\text{CH}-\text{CF}_2\text{Br}$	22
$\text{CH}_2=\text{CBr}-\text{CBrF}_2$	23
$\text{CH}_2=\text{CH}-\text{CF}(\text{Cl})-\text{CF}_2\text{Br}$	24

(Other workers<sup>19</sup> have previously noted that halogens situated on fluorosubstituted carbons, or on saturated carbons immediately adjacent to these, are remarkably inert in nucleophilic reactions. The reaction conditions involved in fire suppression and extinguishment are free radical in nature and thus the relative reactivities of the bromine atoms in the species above would not be expected to parallel the nucleophilic non-reactivities observed by these other workers. It might be predicted that the allylic nature

of bromines in the last two compounds could provide especially high labilities. Attempts will be made to synthesize at least these two candidates in this initial phase of research.)

B. Laboratory testing of fire extinguishabilities of volatile olefinic Halon candidates.

Representative agents, synthesized as described above, will be tested in a cup-burner as described in reference 6; extinguishing concentrations of these will be compared to those of Halons 1211 and 1301.

C. Subsequent project work phases.

1. When the most effective OCFC agents have been identified in the cup-burner tests, non-volatile precursor (NVP) agents (of the families [a - e] in Table I) will be synthesized, using well known techniques described, for example, in reference (7).

2. These precursors will then be pyrolyzed in comparative test conditions to ascertain which precursors would most readily pyrolyze to volatile olefinic halon agents, and in the highest yield.

3. Toxicity studies for both OCFC and NVP/OCFC agent systems will be conducted to ascertain general safety parameters for these systems.

4. Field testing of optimized precursor agent system, in which the optimized precursor agent system will be field tested to ascertain the effectiveness of this agent in open air fire zone conditions as well as in sealed spaces. Attention will be directed to the following areas:

- a. Operational behavior and requirements and environmental emission standards.
- b. Quantities required for effective fire extinguishment, and to streaming and other deliverability parameters.
- c. Thermal stability of the agent at highest anticipated ambient temperatures, to ascertain minimum shelf life under most stringent storage conditions.

"Go/no go" decision points would exist for the overall project at the completion of each of the major phases as described above.

#### PRELIMINARY RESEARCH RESULTS

The first agent to be tested for fire extinguishing capabilities was 4-bromo-3-chloro-3,4,4-trifluoro-1-butene ( $\text{CH}_2=\text{CH}-\text{CF}(\text{Cl})-\text{CF}_3$ ). This compound has proven to be quite effective. Thus, a 5% concentration of this OCFC

extinguishes fires in cup burner tests, as compared with values of 4% for Halon 1211 and 6% values for the alternative Halon 123 mix of current interest. in view of the highly encouraging results of this first effort, other OCFC agents are now undergoing synthesis and will be tested when available in this joint research effort.

#### SIGNIFICANCE OF RESULTS

This study will establish an important direction for future research in development of effective non-volatile Halon fire extinguishing agents which would pose minimal hazards to the environment and firefighting personnel. Such non-volatile olefinic Halon precursors could be formulated as paints, resins, or other coating materials, and also in surfactants for use in firefighting foam formulations for large scale petroleum and petrochemical fire fighting applications.

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