NON-VOLATILE PRECURSORS TO OLEFINIC BROMOFLUOROCARBONS [NVP-OBFCs] AS ALTERNATIVE FIRE EXTINGUISHING AGENTS WITH REDUCED GLOBAL ENVIRONMENTAL IMPACTS

CAPT John Floden
USAF (AFESC/RDCF)
Tyndall AFB, FL 32403-6001

William W. Bannister and Edwin G. E. Jahngen
Dept. of Chemistry,
University of Massachusetts at Lowell
Lowell, MA 01854

Jonathon S. Nimitz
New Mexico Engineering Research Institute
Albuquerque, NM 87106-4339

Responsible scientific organizations have determined that commercial chlorofluorocarbon (CFC) emissions pose serious environmental and health problems in terms of unacceptably high stratospheric ozone depletion potentials (ODPs). This ozone is necessary for protection of life on earth from damaging ultraviolet radiation. CFCs are used as refrigerants, foamblowing 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 have seriously high ODPs. Moreover, both CFCs and BFCs have also been demonstrated to pose unacceptably high global warming potentials (GWPs). (Since these compounds are highly volatile and have very high chemical stabilities, they pass unscathed through lower atmospheric levels and accumulate in the stratosphere. In the lower atmospheric regions these agents prevent passage of infrared radiation from the earth, thus creating the global warming effect. In the stratospheric regions in which agents finally accumulate, the highly energetic ultraviolet radiation from the sun is able to overcome the chemical stabilities of these CFC and BFC agents, causing formation of ozone destroying free radical species which arise from the degradation of these compounds.).

Most emission problems are due to leaks of volatile CFCs from refrigerators and air conditioners. There has also been significant increases in atmospheric concentrations of Halon 1211 from releases from firefighting, firefighter mining, 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.[1,2,3,4,5,6,7]

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 use Halon fire extinguishing agents:[6]

1. Halon agents in current use (especially Halons 1211 and 2402) have high enough toxicities to cause human deaths.

2. Gaseous Halons have poor deliverability.

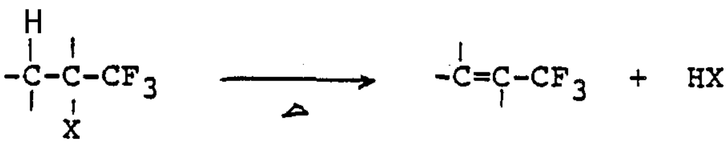
3. Gaseous Halons do not provide good security (i.e., these dissipate rapidly) when applied to burning liquids.

It was also postulated that olefinic bromofluorocarbon (OBFC) agents (though not yet available in bulk) could serve as superior new generation alternative Halon extinguishing agents.

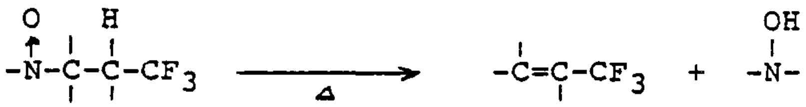
A variety of approaches exist for synthesis of olefins, including thermal degradations of halides, amine oxides, ammonium salts, alcohols, and esters. (See Table I.)

TABLE I. THERMAL DEGRADATION SCHEMES[8]

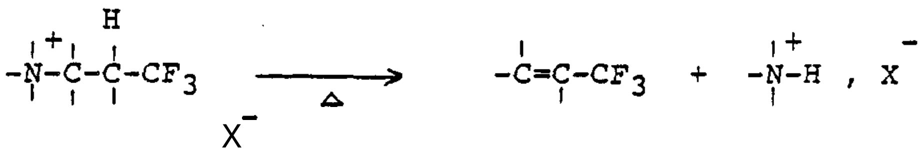
a. **Dehydrohalogenation of haloalkanes**



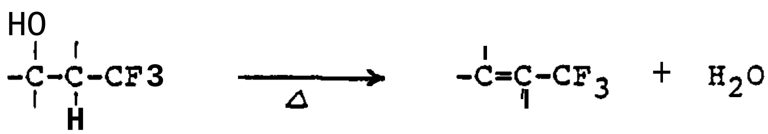
b. **Amine oxide eliminations ("Cope")**



c. Ammonium **halide eliminations ("Hofmann")**



d. **Dehydration of alcohols**



e. **Ester pyrolysis ("Bailey")**

These pyrolytic schemes can also provide a basis for considerable superiority over current Halon agents. Thus, if a non-volatile precursor (NVP) is selected as the extinquishing agent, which would then thermally decompose to form the OBFC, the non-volatility of the precursor would provide many important and unique advantages:

1. In view of the high chemical stabilities and volatilities of the Halons, which lead to their high ODP and GWP values, the approach which has received almost exclusive attention in searching for Halon alternatives has been to synthesize agents with decreased stabilities. With lack of chemical stability, it was felt that the new Halon alternative could not survive ascent into the stratosphere, and could not thereby pose ODP problems. The most important alternatives thus far investigated have been HCFC agents, CFCs with one **or** more hydrogen atoms which significantly reduce chemical stability for these agents. Unfortunately, it has become increasingly apparent that the chemical stabilities are still sufficiently great **as** to continue to pose significant ODP problems. It is unlikely that regulatory commissions will permit use of such agents beyond the year 2000 for any purpose, including fire extinguishment9

   This use of a non-volatile precursor (NVP), which would thermally degrade in the heat of a fire zone to form an effective olefinic bromofluorocarbon (OBFC) fire extinguishing agent, provides a new approach to the problems of ozone depletion and global warming. Being non-volatile, there would be essentially no accumulation of this **type** of agent at any atmospheric level; hence, there would be no GWP or ODP concerns.

2. Although the Halons themselves are safe in terms of vapor hazards, recent evidence indicates that HCFC vapors **are** mutagenic and unacceptably **toxic.**[10] This poses serious problems for fiiefighters who would be exposed on a routine basis to such materials. The NVP/OBFC agents we **are** proposing would have essentially no vapor hazard.

3. The highly volatile Halon and HCFC agents have very limited range of delivery when directed onto fires from pressurized hoses. Most of the agent vaporizes enroute to the fire, particularly **as** the agent approaches the heat of the fii; typically, more than 90% of the agent is lost without effect en route to the fie. This constitutes serious problems in terms of toxicity, ODP and GWP, and expense

considerations. Moreover, firefighters must apply these types of agents at very close range to the fire, with great hazards due to flame and possible explosion effects. The excellent streaming effects of the proposed liquid NVP/OBFCs would provide drastically reduced agent requirements, and greatly increased range for delivery onto fires.

4. It has recently been reported[11] that the new HCFCs currently undergoing research and development for possible use as fire extinguishing agents **may themselves be dangerously flammable under certain conditions of high heat.** Although this may also be true for OBFCs and NVP/OBFCs, the danger would be considerably less. Thus, as indicated above, Halons and HCFCs are so highly volatile that these agents must be applied in very large excess in order to ensure that adequate concentrations will actually develop in fire zones; but delivery requirements for non-volatile NVP/OBFC agents would be very much smaller. Hence, any anomalous flammability problems which could conceivably develop would be minimized for the NVP/OBFC agents.

5. After extinguishment of the lire, there would still be residual NVP/OBFC which would still be pyrolyzing to OBFC agent as a result of hot surface contact. This should Serve to prevent flash back fire effects which frequently arise after initial extinguishment of fires.

GENERAL OBJECTIVES OF THE PROPOSED RESEARCH PROJECT

Objectives of the overall project have been to synthesize, test and evaluate a series of olefinic Halon precursors. These would generate OBFCs by thermal decomposition specifically and only in zones heated by flame activity. Thus, the volatile OBFC that would function as the actual extinguishing agent would be produced only when and where needed, by pyrolytic decomposition of the non-volatile precursors (NVPs).

INCORPORATION OF NVP/OBFC AGENTS INTO AFFF FORMULATIONS

One of the greatest problems in use of Halon or HFCF fire extinguishing agents is delivery onto fire zones, due to the very high volatility of these agents and the very high rate of evaporation in the trajectory. Even if solid streams of these volatile agents are projected from a nozzle, these quickly degenerate into small droplet size sprays and vapor clouds, with drastic reduction in trajectory range, and drastic increase in blast and thermal hazard to firefighters. By using non-volatile precursor agents, a capability arises for incorporation of very small but very effective concentrations of the NVP/OBFC agent in an AFFF formulation which can be delivered at greatly increased range onto the fire zone.

Surfactants used in AFFF have unique capabilities for enhancing rates of thermal decompositions of NVP/OBFC agents to form OBFCs. Thus, 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.[12,13,14] (See Figure 1.)

It has been shown by members of this group[15] and by others[16-21] that water <u>stabilizes</u> reactants as are cited in Table I, which can be pyrolized to form olefinic decomposition products. Moreover, we have shown that when molecules with these groups are emulsified into the anhydrous interiors of surfactant micelles, decomposition rates are greatly increased. Thus, a feasibility exists to develop NVP/OBFC formulations which could be stored for long periods of time without decomposition. When added to an AFFF agent and emulsified in water and heated, these agents would quickly and easily decompose to form an OBFC extinguishing agent when applied to a hot fire zone in an AFFF hose stream. (See Figure 2.)

Since no agent is lost by evaporation in trajectory into the fire zone, agent amounts needed for effective firefighting would be drastically reduced. Only that portion of the agent which actually contacts the hot fire zone would emit volatile OBFC, reducing Halon emissions very significantly, and with concomitant increases in agent security. Also, since acute toxicity effects of volatile agents tend to be more severe for nonvolatile materials, toxicity problems posed by exposure of firefighters would be greatly reduced.

Figure 1. Micellar emulsification of NVP materials in AFFF.

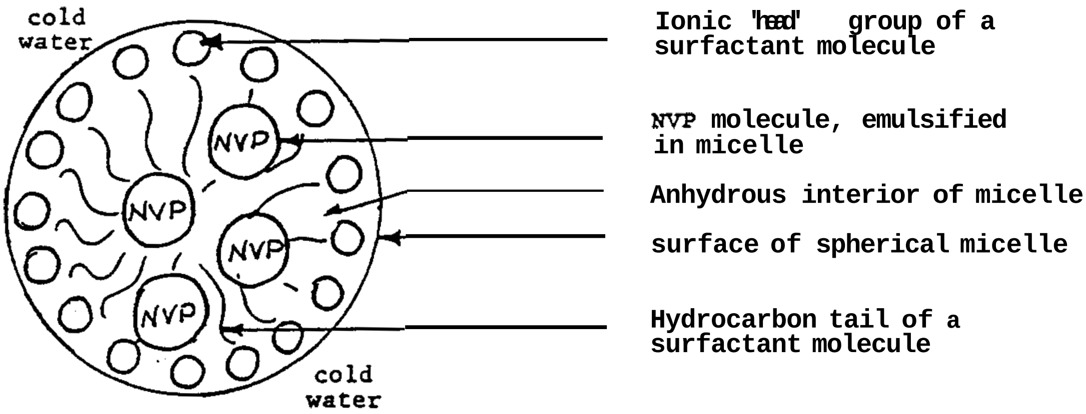
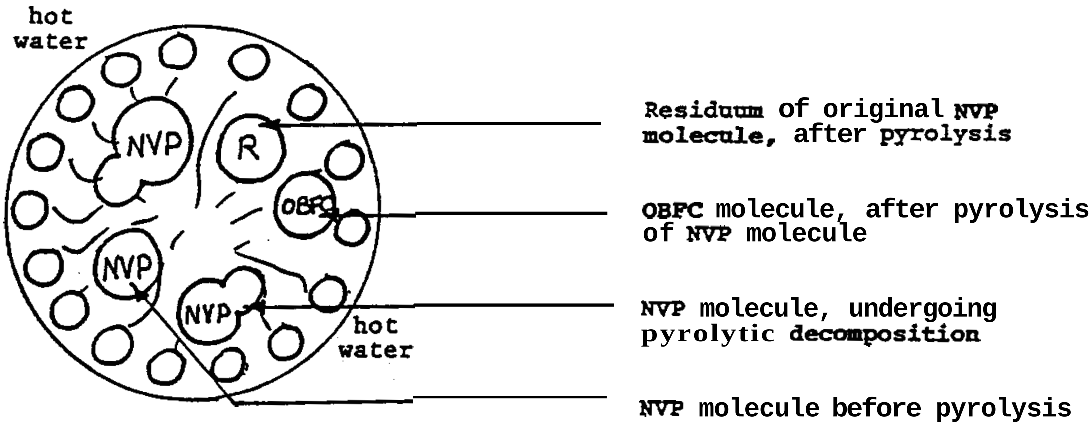


Figure 2. Micelle catalyzed pyrolysis of emulsified NVPs.



RESULTS OF WORK THIS FAR PERFORMED ON THIS PROJECT

Some preliminary work on the overall project has already been performed, under auspices of the *Air* Force Office **of** Scientific Research. Two agents were synthesized for initial testing and comparison **of** extinguishing capabilities with those of Halon **1211** and HCFC **123.** The results of cup burner tests(performed at the New Mexico Engineering Research Institute **are** shown in Table II. (It should be noted that the lower the cup burner test result, the more efficient the fire extinguishing capability **for** the agent. Thus, the two OBFC agents which were first to be studied in the program appear to have fire extinguishing capabilities better than that of the Halons in widest use today as fire extinguishing agents.)

TABLE 11. OBFC CUP BURNER RESULTS AND COMPARISONS

	Concentration for fire extinguishment
CH_2=CH-CF (Cl) -CF_2Br	**4.5 %**
CH_2 CH CF2 CF_2Br	**3 %**
CF_2BrCl (Halon **1211)**	**5 %**
CF_3CHCl_2 (HCFC **123)**	**6 %**

SIGNIFICANCE OF RESULTS

This study will establish an important direction for future development of effective non-volatile Halon fire extinguishing agents with minimal hazards to the environment and firefighting personnel. Such non-volatile olefinic Halon precursors could be formulated in *AFFF* surfactants for **use** in firefighting foam formulations for large scale petroleum and petrochemical fire fighting applications, and also in paints, resins, or other coating materials. In all applications, there would be little or no OBFC emissions to the atmosphere due to fire extinguishing operations, or to **tank** leakages, inadvertent valve openings, and similar sources of accidental releases which currently pose enormous environmental problems. NVP/OBFC agents would be **as** "clean" as *AFFF* formulations: there is no residue from heat or combustion. At least some NVP/OBFC agents (e.g., quaternary ammonium salts) could show anti-corrosion activity for exposed metal surfaces. Use requirements **and** toxicities for NVP/OBFC agents may be drastically reduced relative to Halons or

HCFCs. Extended throw ranges for these non-volatile agents should result in greatly increased safety for firefighting personnel who could thereby direct these extinguishing agents at much greater distances from the fire.

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