



NRL/MR/6185--97-7961

Extinction Studies of Polyfluoropropanes and Halons in Methane/Air and Propane/Air Counterflow Diffusion Flames

BRADLEY A. WILLIAMS
JAMES W. FLEMING
RONALD S. SHEINSON

*Combustion Dynamics Section
Navy Technology Center for Safety and Survivability
Chemistry Division*

June 27, 1997

19970710 068

DTIC QUALITY INSPECTED 4

Approved for public release; distribution is unlimited

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (<i>Leave Blank</i>)		2. REPORT DATE June 27, 1997	3. REPORT TYPE AND DATES COVERED Interim Report 10/96 — 3/97	
4. TITLE AND SUBTITLE Extinction Studies of Polyfluoropropanes and Halons in Methane/Air and Propane/Air Counterflow Diffusion Flames			5. FUNDING NUMBERS 61-3594-0-7	
6. AUTHOR(S) Bradley A. Williams, James W. Fleming, and Ronald S. Sheinson				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Research Laboratory Washington, DC 20375-5320			8. PERFORMING ORGANIZATION REPORT NUMBER NRL/MR/6185--97-7961	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Naval Sea Systems Command (Code 03R) 2531 Jefferson-Davis Highway Arlington, VA 22242-5160			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (<i>Maximum 200 words</i>) Several fluoropropanes have been tested for fire suppression in methane/air and propane/air diffusion flames. The agents were added to the air stream, and the variation in the air stream extinction flow rate as a function of agent concentration was recorded. Significant isomeric differences were observed in suppression effectiveness of the penta-, hexa-, and heptafluoropropanes. The agents' effectiveness depended principally on the number of CF ₃ groups in the molecule. The most efficient fluoropropane agents were perfluoropropane (FC-218), 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea), and 1,1,1,3,3,3-hexafluoropropane (HFC-236fa), all with two CF ₃ groups. The fluorine/hydrogen ratio in the agent was found to have only a minor effect on suppression, with a higher fluorine content producing slightly better inhibition at low agent concentrations. The relative rankings of the agents were essentially identical for methane and propane fuels. Cup burner tests of HFC-227 and HFC-236 isomers with n-heptane and methanol fuels find the same isomeric differences. These observations indicate that hydrofluorocarbons possess a significant chemical suppression of combustion, and that CF ₃ groups are critical to this suppression. In the propane/air flames, four halons were also tested: CF ₃ Br, CF ₃ I, CF ₂ ClBr, and CHF ₂ Br. The relative effectiveness of these agents also demonstrates a significant chemical effect of CF ₃ groups.				
14. SUBJECT TERMS Fire suppression Halon Fluorocarbon Combustion			15. NUMBER OF PAGES 18	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

CONTENTS

BACKGROUND	1
PRESENT STUDY	2
EXPERIMENTAL PROCEDURE	4
RESULTS	6
DISCUSSION	12
CONCLUSIONS	14
ACKNOWLEDGMENTS	15
REFERENCES	15

EXTINCTION STUDIES OF POLYFLUOROPROPANES AND HALONS IN METHANE/AIR AND PROPANE/AIR COUNTERFLOW DIFFUSION FLAMES

BACKGROUND

Polyfluoropropanes are being developed as replacements for bromine- and chlorine-containing firefighting agents which deplete stratospheric ozone. These hydrofluorocarbons contain no chlorine, bromine, or iodine, and therefore have negligible ozone depletion potential. They do, however, have appreciable infrared absorption, and thus can be significant global warming agents depending on their atmospheric lifetime.

1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea, Great Lakes FM-200™) will be used on the next class of U.S. Navy ships (LPD-17). 1,1,1,3,3,3-hexafluoropropane (HFC-236fa, Dupont FE-36™) and perfluoropropane (FC-218, 3M CEA-308™) are also marketed as firefighting agents. All of these agents are less efficient than Halon 1301 (CF₃Br), in terms of the volume and weight of agent required to provide protection for a given space. This increase in the size and weight of the fire protection system is undesirable in a shipboard application. While it is feasible to allow for increased fire protection system space and weight in newly constructed ships, such requirements rule out usage as a back fit halon replacement in most cases. There exists a need to find improved, environmentally friendly agents. The present study compares the suppression effectiveness of a number of fluoropropane and halon agents. The goals of this study are to identify chemical structures leading to efficient fire suppression, and to use this knowledge to propose new, more efficient agents.

Fire suppression occurs by a combination of physical (primarily heat capacity) and chemical (reduction of radicals important in flame propagation) mechanisms. Agents such as water and carbon dioxide which are chemically inert in flame environments are purely physical in their suppression mechanism. The suppression effectiveness of CF₃Br has been identified as being principally due to catalytic scavenging of flame radicals by the bromine atom [1]. To a lesser extent, the relatively high heat capacity of Halon 1301 also contributes to suppression, and the CF₃ group also contributes some chemical suppression [2,3]. The hydrofluorocarbons' lack of bromine accounts for their lower suppression effectiveness. The fire suppression of fluorinated propanes is due to their heat capacity and chemical suppression by fluorine.

PRESENT STUDY

We have tested eight polyfluoropropanes (all containing at least five fluorine atoms) in both methane/air and propane/air counterflow diffusion flames. The compounds tested are listed in Table I. They include octafluoropropane, the two isomers of heptafluoropropane, three of the four isomers of hexafluoropropane, and two of the five isomers of pentafluoropropane. As a general rule, hydrofluorocarbons tend to be flammable unless they contain more fluorine atoms than hydrogen atoms. Therefore only fluoropropanes containing at least five fluorine atoms are likely to be useful extinguishment agents. It has been previously noted that the presence of CF_3 groups is significant in chemical inhibition by fluorocarbons [2,3]. Of the compounds tested, three have CF_3 groups on both ends of the molecule, four have one CF_3 group, and one (HFC-245ca) has no CF_3 groups.

Table I: Fluoropropanes Tested in Present Study

Name	Trade name	HFC #	CAS #	Structure
octafluoropropane	CEA-308 (3M)	218	76-19-7	$\text{CF}_3\text{CF}_2\text{CF}_3$
1,1,1,2,2,3,3-heptafluoropropane		227ca	2252-84-8	$\text{CF}_3\text{CF}_2\text{CHF}_2$
1,1,1,2,3,3,3-heptafluoropropane	FM-200 (Great Lakes)	227ea	431-89-0	$\text{CF}_3\text{CHFCF}_3$
1,1,1,2,2,3-hexafluoropropane		236cb	677-56-5	$\text{CF}_3\text{CF}_2\text{CH}_2\text{F}$
1,1,1,2,3,3-hexafluoropropane		236ea	431-63-0	$\text{CF}_3\text{CHFCHF}_2$
1,1,1,3,3,3-hexafluoropropane	FE-36 (Dupont)	236fa	690-39-1	$\text{CF}_3\text{CH}_2\text{CF}_3$
1,1,2,2,3-pentafluoropropane		245ca	679-86-7	$\text{CHF}_2\text{CF}_2\text{CH}_2\text{F}$
1,1,1,2,2-pentafluoropropane		245cb	1814-88-6	$\text{CF}_3\text{CF}_2\text{CH}_3$

The heat capacities of hydrofluorocarbons tend to increase with each additional fluorine atom, due to the C-F stretching frequencies becoming equipartitioned at a lower temperature. Our calibration procedure for the mass flow meter gave relative values for the heat capacities of the different agents. We found that the heat capacities at room temperature increased by roughly 5% for each fluorine atom. Among different isomers having the same chemical formula, differences in heat capacity were within the calibration uncertainty of $\pm 2\%$. Differences in observed suppression efficiency among different agents, particularly between isomers, are therefore indicative of chemical rather than physical suppression.

For comparison, four halons containing bromine or iodine were also tested in the propane/air flame. These include CF_3Br (Halon 1301, BFC-13B1), CF_3I (Halon 13001, FIC-

1311), CHF₂Br (Halon 1201, HBFC-22B1, Great Lakes FM-100™), and CF₂ClBr (Halon 1211, BCFC-12B1). Two of these agents contain a CF₃ group.

The selected agents were tested in a counterflow diffusion burner. The burner consists of two tubes 1 cm in diameter pointed towards one another through which the fuel and air flow [4,5]. The ends of the two tubes are aligned and are separated by 1 cm. A diffusion flame can be stabilized in the mixing region between the two tube exits. The position of the flame can be adjusted by changing the relative gas flow velocities through the two tubes. For fuel/air flames, the flame zone generally appears on the air side of the stagnation plane, the position where the axial velocity component is zero. Each tube has a surrounding collinear tube in which a shroud flow of inert gas can be introduced, although no shroud flow was used in the present study. Velocimetry measurements of the axial velocity as a function of radial position near the tube exit shows that the velocity profile is nearly parabolic:

$$v_z(r) = V_0(1-(r/a)^2) \quad (1)$$

where V_0 is the velocity along the centerline at the tube exit, r is the radial position, and a is the tube diameter.

As the flow rates of fuel and air are increased, the flame will extinguish when the flow velocities of the gases become so large that the flame is unable to maintain a steady position (i.e., the flame is blown out). This extinction condition can be quantified in terms of the *extinction strain rate*, meaning the maximum velocity gradient along the tube centerline on the air side of the flame at the point of extinction. The strain rate is typically specified along the air side in order to facilitate comparisons between flames of fuels with different molecular masses. Determination of the strain rate requires measurement of the gas velocity field by a technique such as laser-Doppler anemometry. The extinction condition can also be quantified in terms of the extinction flow rate, although this value will be dependent on the geometry of the experimental apparatus, whereas the extinction strain rate is a fundamental property of a given fuel/oxidizer system and is apparatus-independent.

We have previously performed laser-Doppler anemometry measurements of methane/air flames, both uninhibited and inhibited by CF₄ and CHF₃ [5]. The value obtained for the extinction strain rate of the uninhibited methane/air flame ($405 \pm 25 \text{ s}^{-1}$) is in good agreement with the values reported by other researchers. We have also shown that in our apparatus, the strain rate is nearly proportional to the air stream flow rate. Since the latter quantity can be measured much more easily, we report here extinction in terms of the flow rate. This is sufficient for comparisons between different agents in the same experimental apparatus.

When an agent is added to the flame, the extinction flow rate (and strain rate) decreases to a lower value. Plotting the changes in the extinction flow rate as a function of the agent concentration gives a picture of the agent's performance. The more effective the agent, the greater the drop in extinction flow rate for a given concentration of agent. Using a counterflow

burner, one can study extinction for a variety of strain rates and agent concentrations. At the lowest flow rates, the counterflow extinction concentrations can be compared to cup burner values. Although the strain rate can be varied in a cup burner, it is always so low that it does not contribute significantly to extinction, and one measures an extinction concentration based on the effect of the agent alone.

The five hepta- and hexafluoro agents were also tested in a cup burner with n-heptane fuel, and three agents (HFC-227ea, HFC-236fa, and HFC-236ea) were tested in the cup burner with methanol fuel. The purpose of these tests was to make the same isomeric comparisons in the cup burner as in the counterflow burner, and to determine if the same trends were evident. The methanol fuel was tested as well as the n-heptane because methanol is a major fire threat in shipboard flammable liquid storage rooms (FLSR). Methanol fires have been previously observed to require much higher concentrations of agent to extinguish than do fires of n-heptane, so the presence of methanol may dictate the design concentration of agent required to provide protection for an FLSR. Fuels such as JP-5 and JP-8 are similar to n-heptane in their extinguishment characteristics.

EXPERIMENTAL PROCEDURE

For flames of methane/air, the fuel flow (typically 1-5 liters/minute) entered the flame region through the top tube, while the air (typically 0.5-3 liters/minute) entered through the bottom tube. A flow of nitrogen (10-15 liters/minute) was added to the combustion chamber to prevent unburnt fuel in the exhaust gas from igniting upon entering the fume hood. For propane/air flames, running the burner in the same configuration produced a flame which was rather unstable, since propane is heavier than air. Because of this buoyancy instability, the propane flame was run in all the tests reported here with the air entering through the top tube, and the fuel through the bottom. In all tests, agents were added to the air stream. This mode of application most closely resembles the application of a total flooding agent in a fire situation, in which the agent will be introduced into the room air in a certain concentration and the fuel is burning as a diffusion flame.

The flow rates of fuel, air, and agent were monitored by mass flow controllers (Sierra Instruments) which were calibrated by a piston flowmeter (Dry-Cal, Bios International). The stated accuracy of the flow controllers is $\pm 1\%$ of full scale. The minimum flow rate at which extinction could be studied was dictated by the precision of the flow controllers. The calibration tests of the flow controllers provided relative values for the room temperature heat capacities of the different agents. For the fluoropropanes, heat capacities increase by some 5% for each fluorine atom substitution (i.e., the HFC-227s have about 5% higher heat capacities than the HFC-236s). Different isomers of the same chemical formula have identical heat capacities within the uncertainty of the calibration.

The agents were obtained from the following suppliers: FC-218 and CF₃Br, Matheson; HFC-227ea, Great Lakes; HFC-236fa and HFC-236ea, Dupont; CHF₂Br, Halocarbon Corp; CF₃I, Flura Corp. The remaining agents were from PCR. The stated purity of the agents was at least 97%; they were used without further purification. All agents were used "neat" with the exception of HFC-245ca. Since this compound has a boiling point near room temperature, it was mixed with air in a 1:3 ratio in order to provide a sufficient backing pressure to provide a stable flow.

The flame was lit by a retractable spark ignitor with only fuel and air flowing. For extinguishment tests of the uninhibited flame, the fuel and air flow rates were slowly increased. The relative flows of fuel and air were adjusted so that the visible flame zone was maintained midway between the two tubes. Since the overall stoichiometry of the fuel + air flow is fuel rich, the flame zone is located slightly to the air side of the stagnation plane (the location where the axial velocity is zero). The flow rates were increased at intervals of 0.4% of full scale (the minimum adjustment interval for the flow meters) at intervals of 20-40 seconds, until the flame extinguished. For the inhibited flames, the flow rates of fuel and air were generally kept constant, and the flow rate of the agent was increased until the flame extinguished. As the flow rate of the agent increased, small adjustments were made to the fuel and air flows to keep the flame midway between the tubes. Increases to the agent were made at intervals of 30-60 seconds, depending on the overall flow rate, in order to allow the concentration of agent in the flame to reach equilibrium between adjustments.

The methane/air flame produced a fairly flat flame with little curvature. The flame went out completely in all extinction studies, with the exception of some tests with the HFC-245 isomers at high concentrations, where an annular flame formed (see below). Propane/air flames had a pronounced upward curvature. Under most conditions, the propane/air flame extinguished in the central region of the flame between the two tubes, forming an annular flame in the shape of a funnel with the small end of the funnel attached to the fuel inlet tube. Complete extinction was only observed in the propane/air flame with the bromine- and iodine-containing agents at concentrations greater than 0.8%. This transition to the annular flame was sometimes observed in the methane/air flame with high concentrations (>6%) of the HFC-245 isomers. Once the flame became annular, it would re-establish itself along the centerline when the flow rates were reduced to about 1 liter/min of both fuel and air with no agent. There is a broad region of bistability where either the curved disk flame or the annular flame can be maintained. Our interpretation of this phenomenon is that the transition to the annular flame does indeed represent extinction, certainly along the centerline where the strain rate is defined for the counterflow flame. The plots of the extinction flow rate as a function of agent concentration below show no evidence of an abrupt change in the cases where the extinction behavior changes from complete extinction to formation of the annular flame.

In the tests with the HFC-245 isomers, particularly in high agent concentrations, a secondary flame zone was observed about 1 mm on the air side of the principle diffusion flame. This appears to be caused by the agents burning as a premixed flame in the air. Although both HFC-245 isomers are considered non-flammable at ambient temperature and pressure, the heat

release from the diffusion flame was apparently sufficient to support their premixed combustion. The secondary flame zone was most pronounced with HFC-245ca, which is much less effective as an agent than HFC-245cb.

The agents HFC-227ea, HFC-227ca, HFC-227ca, HFC-236fa, HFC-236ea, and HFC-236cb were tested in a cup burner apparatus using n-heptane and methanol fuels. The apparatus and methodology are described in detail elsewhere [2,3]. The piston flowmeter was used to measure the agent and air flows after each extinction measurement. The total flow rate of air + agent was 20 ± 1 liters/minute for all measurements, giving a flow velocity of 4.1 ± 0.2 cm/s past the cup. The fuel level in the cup was kept as close as possible to the top of the cup (within 0.5 mm) without overflowing. When the fuel level was approximately 1.5 mm below the cup rim, the flame was stabilized on the rim, leading to extinguishment concentrations which were increased by about 5% relative to that obtained with the liquid level close to the rim.

RESULTS

Figures 1 and 2 show the extinction mass flow rate of the air stream (air + agent) vs. agent volume concentration in air for methane and propane fuels, respectively. Among the polyfluoropropanes, agent extinction curves cluster together in terms of number of CF_3 groups, particularly at high agent concentrations. The agent efficiency does not correlate significantly with any structural feature other than the number of CF_3 groups. The most effective fluoropropane agents are FC-218, HFC-227ea, and HFC-236fa, all of which contain two CF_3 groups. The four agents (HFC-227ca, HFC-236ea, HFC-236cb, and HFC-245cb) which contain only one CF_3 group, are all substantially less effective. For these agents, it takes roughly a 20-30% greater agent flow rate to extinguish a flame at a given fuel/oxidizer flow, compared to the agents with two CF_3 groups. HFC-245ca, which contains no CF_3 groups, is a very poor agent. As seen in the Figures, the extinction flow rate actually increases up to an agent concentration of about 2%, indicating that this compound *promotes* combustion under certain conditions.

Among agents with the same number of CF_3 groups, compounds with higher F:H ratios tend to be slightly more effective agents, particularly at low concentrations. FC-218 is slightly more effective than HFC-227ea and HFC-236fa. Among the compounds with one CF_3 group, HFC-227ca is more effective than HFC-236ea and HFC-236cb, which are in turn more effective than HFC-245cb. At higher agent concentrations, the importance of the F:H ratio diminishes. The effect is in any case quite minor compared to that of CF_3 groups, as evidenced by the fact that HFC-236fa is a more effective agent than HFC-227ca, which has more fluorine atoms but fewer CF_3 groups.

Comparing the plots for the methane/air and propane/air flames, we see that the shapes and relative positions of the curves for the different agents are nearly the same for both fuels. This observation is somewhat different than the comparison between CF_4 and CHF_3 . In that study it

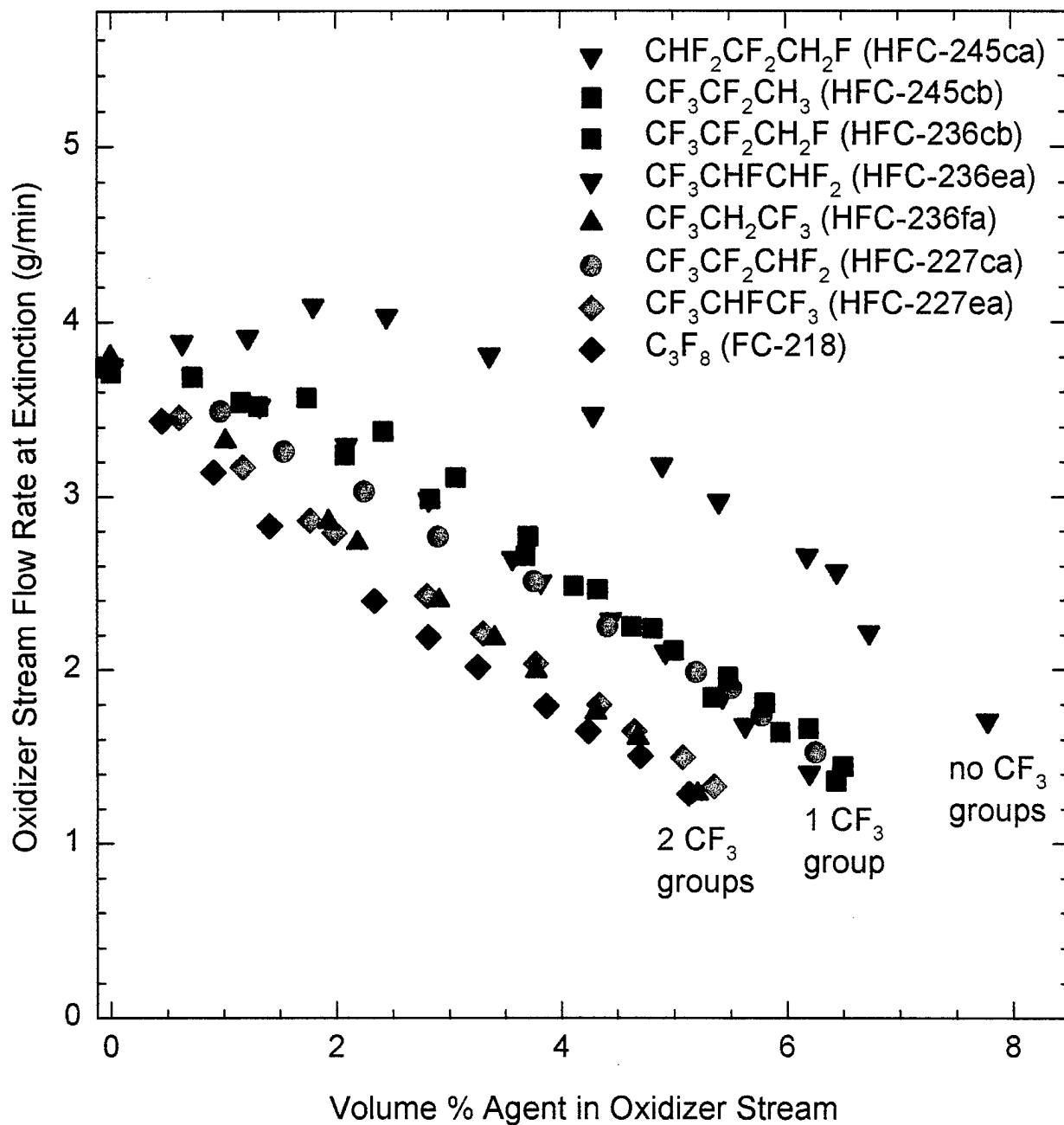


Fig. 1: Extinction flow rate vs. agent concentration in methane/air counterflow flame.

was found that CHF₃ had a higher relative suppression effectiveness compared to CF₄ in a propane flame than in a methane flame.

The uninhibited propane/air flame had a higher extinction flow rate than the uninhibited methane/air flame. The extinction flow rate for the propane/air flame, however, decreased more rapidly upon addition of the agent. The concentration of agent required for a 50% reduction of the extinction flow rate was less in propane/air than methane/air for all agents tested. This may be a consequence of the lower hydrogen:carbon ratio of propane compared to methane [5]. For both fuels, the concentration of the agents with one CF₃ group required for a 50% reduction in extinction flow rate was some 30% higher than for agents with two CF₃ groups. About 90% more HFC-245ca was required for a 50% reduction in extinction flow rate than was required for the fluoropropanes with two CF₃ groups.

Among the agents tested in the propane flame which contain bromine or iodine, the presence or absence of a CF₃ group also significantly influences suppression. CF₃Br is a slightly more effective agent than CF₃I, indicating that bromine has slightly more efficient catalytic activity than iodine. CHF₂Br is much less efficient than CF₃Br, indicating that the CF₃ group in Halon 1301 makes a substantial contribution to the agent's chemical suppression. CF₂ClBr is also slightly less effective than CF₃Br, even though chlorine is itself a catalytic agent (albeit much less efficient than bromine), and therefore, in general, one chlorine atom should contribute more to suppression than one fluorine atom. This comparison highlights the importance of CF₃.

The results obtained in the cup burner for HFC-227ea, HFC-227ca, HFC-236fa, HFC-236ea, and HFC-236cb (Table II) with n-heptane show the same trend as the counterflow data. HFC-236fa appears to be slightly more effective than HFC-227ea; both are much better than the HFC-227 and HFC-236 isomers which have only one CF₃ group. The extinction concentration for HFC-227ea is slightly less than the previously reported value [6] of 6.6%.

Table II: Cup Burner Data for HFC Agents using n-Heptane Fuel

Agent	Number of Measurements	Extinguishing Concentration (vol. % in air)	Standard Deviation (vol. % in air)
HFC-227ea	10	6.4	0.1
HFC-227ca	5	6.9	0.1
HFC-236fa	7	6.1	0.1
HFC-236ea	7	7.2	0.2
HFC-236cb	4	7.4	0.1

For the three agents tested in the cup burner with methanol fuel, extinction concentrations were significantly higher than with n-heptane. The relative ranking of the agents was the same: HFC-236ea, with one CF₃ group, was less efficient than both HFC-227ea and HFC-236fa, with two CF₃ groups. One difference noted between the two fuels is that there appears to be a larger difference in effectiveness between HFC-236fa and HFC-227ea with methanol (0.9%) than with n-heptane (0.3%). The reason for this trend is not clear; the difference in the relative extinguishment concentrations is slightly outside the uncertainties in the measurements.

Table III: Cup Burner Data for HFC Agents using Methanol Fuel

Agent	Number of Measurements	Extinguishing Concentration (vol. % in air)	Standard Deviation (vol. % in air)
HFC-227ea	6	8.9	0.1
HFC-236fa	6	8.0	0.2
HFC-236ea	6	9.9	0.2

The extinction flow rate plots taken in the counterflow burner for the agents which contain Br or I show a pronounced upward concave curvature, whereas in the plots for the hydrofluorocarbons (particularly those with two CF₃ groups), the extinction flow rates decrease almost linearly with agent concentration. In cup burner extinction studies performed with mixtures of different agents, it is found that when a chemical catalytic agent such as CF₃Br is mixed with a purely physical agent such as CF₄ or SF₆, there is a nonlinear additivity of the two agents' effects [7-9]. A small amount of a catalytic agent has a disproportionate effect on flame extinction. This nonlinearity has been interpreted as being due to saturation of the catalytic effect (chain recombination of radicals) as the amount of agent increases, and taken as a signature of chemical catalytic inhibition [9].

The shape of the plots in Fig. 2 for the agents containing Br or I indicate that the inhibition efficiency is concentration dependent. The counterflow data appear to manifest the catalytic saturation phenomenon observed in the cup burner studies, although this interpretation may need to be refined if the temperature profiles near extinction are markedly different in the inhibited and uninhibited flames. The extinction plots for the HFC agents with one or no CF₃ groups show an upward-convex curvature, particularly at small loadings. It is tempting to invoke a *promoting* effect (production of radicals) for these agents, although their combustion chemistry is undoubtedly much more complicated than the single catalytic cycle responsible for the inhibition effect of bromine and iodine. If a cup burner study using a mixture of HFC-245ca and SF₆ were to show that the mixture was *less* effective than the sum of its constituents, this would be evidence for such a promoting effect.

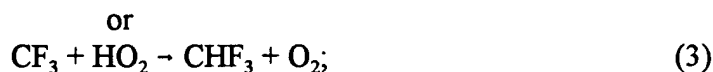
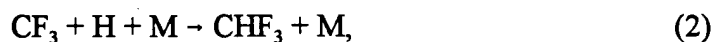
DISCUSSION

Both the counterflow and cup burner extinction data highlight the effect of CF_3 groups, among bromine and iodine containing agents as well as HFCs. This finding is consistent with the previous analysis performed in our laboratory which attributed 25% of the inhibition effectiveness of Halon 1301 to the chemical inhibition by CF_3 [2]. Workers at New Mexico Engineering Research Institute (NMERI) have performed cup burner measurements on three sets of HFC isomers [10]: HFC-227ea and HFC-227ca, HFC-236fa and HFC-236ea, and HFC-134 (CHF_2CHF_2) and HFC-134a ($\text{CF}_3\text{CH}_2\text{F}$). In all cases, the isomer with the larger number of CF_3 groups gave a lower value for the extinction concentration. The cup burner data, both from NRL and elsewhere, are consistent with the counterflow data regarding the effect of CF_3 groups.

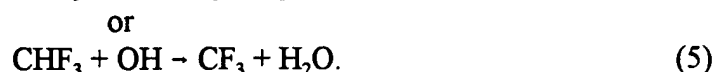
Brabson, *et al.* [11] recently investigated chemical inhibition due to CF_3 groups by comparing the effects of CHF_3 and CF_4 added to premixed methane/air flames. The study concluded that once the effect of CHF_3 on the equivalence ratio was taken into account, the two agents exhibited essentially the same behavior, indicating that the chemical suppression by CHF_3 is minor. CF_4 has little or no chemical suppression because very little of it decomposes in most flame environments. Previous data in our counterflow burner [5] indicates that CHF_3 and CF_4 do indeed have similar extinction characteristics in methane/air flames, but that CHF_3 has significantly greater effectiveness than CF_4 in propane/air flames. NRL cup burner measurements using n-heptane also show CHF_3 to be more effective than CF_4 [3,12]; these data indicate a significant chemical contribution to CHF_3 suppression in both propane and heptane flames, which is apparently lacking in methane. In contrast, all of the fluoropropanes have the same relative effectiveness for both propane and methane fuels (note that none of them is a purely physical agent as is CF_4). It is not clear why CHF_3 seems to have little net chemical suppression in methane flames. Since the H:C ratio in methane is much higher than for most other fuels, the methane flame may produce more atomic hydrogen and therefore be more difficult to chemically suppress. CHF_3 may also be a relatively ineffective chemical agent due to its high stability. Since the C-H bond in CHF_3 is much stronger than the C-C bonds in the fluorinated propanes, the CF_3 radical may not be formed from trifluoromethane in low temperature regions of the flame, which may diminish chemical suppression.

The larger question is why CF_3 groups are so important in suppression. Since CF_3 groups have a uniform effect in suppression among all the fluoropropanes studied, it is almost certain that CF_3 is evolved as a radical species in the breakdown of all these compounds. One anomalous feature of the CF_3 radical is that it has a relatively low dissociation energy. While C-F bonds in most compounds have dissociation energies in the range of 120-130 kcal/mole, the dissociation energy of CF_3 is only about 80 kcal/mole [13]. This characteristic may be important in chemical suppression, since it means that one F atom is easily available to scavenge a hydrogen atom.

Another possibility which has been suggested [14] is that there may be a catalytic cycle involving CF_3 and CHF_3 :



followed by:



The net effect is to recombine two radicals. In ref. [11], the authors discounted this possibility based on the observed lack of chemical effect of CHF_3 on the propagation speed of premixed methane flames. It may be the case, however, that the inhibition mechanism is different in non-premixed flames. The catalytic cycle, while speculative, cannot be discounted.

The present data do not, unfortunately, provide a definitive explanation for the effectiveness of CF_3 . Studies in a variety of flame environments will be needed to answer this question, particularly comparisons between premixed and non-premixed flames as well as studies over a range of pressures, since reactions (2) and (3) are more likely to be favored at higher pressures. Validated kinetic models for fluoropropane flame chemistry would shed light on the source of the chemical effect.

Since compounds with more CF_3 groups tend to have higher suppression effectiveness, the question arises whether an agent can be designed which has three or more CF_3 groups. There are several difficulties in accomplishing this goal. To be a viable total flooding agent, a compound must have a boiling point below room temperature. Most fluoropropanes and some fluorobutanes meet this goal, but fluorinated pentanes and higher hydrocarbons do not. The fluorobutanes which contain three CF_3 groups are perfluoroisobutane, $\text{CF}(\text{CF}_3)_3$, and 2-(trifluoromethyl)-1,1,1,3,3,3-hexafluoropropane, $\text{CH}(\text{CF}_3)_3$. Both of these compounds have acceptably low boiling points, but are problematic for other reasons. Perfluoroisobutane will probably have a very long atmospheric lifetime and hence a high global warming potential since it is perfluorinated and therefore not subject to OH radical attack in the troposphere. For this reason its use is likely to be severely restricted, as are other perfluorocarbons. It may, however, be a superior agent to perfluoro-*n*-butane, which is used in applications where very low agent toxicity is required.

$\text{CH}(\text{CF}_3)_3$ is unlikely to be a viable agent because it may tend to form perfluoroisobutylene, $\text{CF}_2=\text{C}(\text{CF}_3)_2$ in the course of its reaction in a flame environment. Perfluoroisobutylene is highly toxic and therefore use of $\text{CH}(\text{CF}_3)_3$ would probably pose an unacceptable risk to personnel. In fact $\text{CH}(\text{CF}_3)_3$ is itself listed as being toxic, although this may result from an impurity of perfluoroisobutylene produced in its synthesis. Perfluoroisobutane does not share this

drawback, since its most likely decomposition pathway involves breaking of a C-C bond, which precludes the formation of perfluoroisobutylene.

Among hydrofluorocarbons, there does not appear to be an agent with three CF_3 groups that will be acceptable in terms of environmental impact and toxicity. However, tris(trifluoromethyl)amine, $\text{N}(\text{CF}_3)_3$, may be an attractive candidate. Due to its structure, it cannot possibly form perfluoroisobutylene, and its toxicity is likely to be low, since perfluorinated amines, unlike their hydrocarbon counterparts, are not bases. Flame inhibition studies with fluorinated amines (although not this particular compound) indicates that they are less efficient than Halon 1301, but are significantly better than HFC-227ea [14]. It has been suggested that fluorinated amines may be more efficient agents than their fluorocarbon counterparts due to the relative weakness of the C-N bond, leading to formation of CF_3 radicals in lower temperature regions of the flame [14].

The atmospheric lifetime of $\text{N}(\text{CF}_3)_3$ is one major issue which needs to be addressed before this compound can be considered as a firefighting agent. Since tris(trifluoromethyl)amine is non-polar and has no hydrogen atoms, it is unlikely to be subject to radical attack in the troposphere. However, $\text{N}(\text{CH}_3)_3$ absorbs ultraviolet radiation in the same wavelength range as do CFCs [15]. If the absorption region is not greatly different for the fluorinated analog, breakdown by ultraviolet radiation might be the dominant removal process, giving a lifetime on the same order as that of CFCs: 50-100 years. The lifetime of fluorinated amines will almost certainly be much less than that of perfluorocarbons, but a more precise determination will require a detailed investigation of their photochemistry, as well as consideration of other possible removal mechanisms.

CONCLUSIONS

The most important observation in the present study is that among polyfluoropropanes, the presence of CF_3 groups is the dominant factor in determining a compound's fire suppression effectiveness. In contrast, the overall F:H ratio in the agent has relatively little effect on the agent's suppression characteristics, at least among compounds with an F:H ratio greater than unity. HFC-227ea ranks with FC-218 and HFC-236fa (all with two CF_3 groups) as the most effective fluoropropanes. Of these three compounds, FC-218 is slightly more effective than the other two compounds (on a molar basis) but has a very long atmospheric lifetime and consequently a high global warming potential. HFC-227ea and HFC-236fa are essentially equal in effectiveness. HFC-227ea has a shorter atmospheric lifetime and lower boiling point than HFC-236fa, so it is likely to be preferable in terms of environmental impact and also discharge characteristics in a total flooding scenario. Among the compounds examined, the Navy's selection of HFC-227ea for the LPD-17 class of ships is supported by the results of this study.

ACKNOWLEDGMENTS

This work was supported by the Naval Sea Systems Command. We acknowledge the provision of HFC-236fa and HFC-236ea by Dupont, HFC-227ea by Great Lakes, and HBFC-22B1 by Halocarbon Corp.

REFERENCES

1. Westbrook, C. K., "Inhibition of Hydrocarbon Oxidation in Laminar Flames and Detonations by Halogenated Compounds," *Nineteenth Symposium (International) on Combustion* (The Combustion Institute, Pittsburgh, 1982), pp. 127-141.
2. Sheinson, R. S., Gellene, G. I., Williams, F. W., and Hahn, J. E., "Quantification of Fire Suppressant Action on Liquid Pool Fires," 1978 Fall Technical Meeting, Eastern States Section, The Combustion Institute, Nov. 29 - Dec. 1, 1978, Miami Beach, FL.
3. Sheinson, R. S., Penner-Hahn, J. E., and Indritz, D., "Physical and Chemical Action of Fire Suppressants," *Fire Safety Journal* **15**, 437-450 (1989).
4. Papas, P., "An Additive Approach to Supersonic Combustion: Use of Silane in Hydrogen-Air Systems and Consideration of Pyrophoric Metals" Ph. D. Thesis, 2005-T, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ (1993).
5. Papas, P., Fleming, J. W., and Sheinson, R. S., "Extinction of Nonpremixed Methane- and Propane-Air Counterflow Flames Inhibited with CF_4 , CF_3H , and CF_3Br ," *Twenty-sixth Symposium (International) on Combustion* (The Combustion Institute, Pittsburgh), in press.
6. Baldwin, S. P., Brown, R., Burchell, H., Eaton, H. G., Salmon, G., St. Aubin, J., Sheinson, R. S., and Smith, W. D., "Cup Burner and Intermediate Size Fire Evaluation," Proceedings of The 1992 International CFC and Halon Alternatives Conference, Sept. 29-Oct. 1, 1992, Washington, DC, pp. 812-815.
7. Sheinson, R. S., and Driscoll, D. C., "Fire Suppressant Concentration Requirements: Agent Mixtures and Depleted/Enriched Oxygen Concentrations," 23rd International Symposium on Combustion, Orléans, France, 1990, work-in-progress poster P70.
8. Tapscott, R. E., May, J. H., Moore, J. P., Lee, M. E., and Walker, J. L., "Next Generation Fire Extinguishing Agents Phase II - Laboratory Tests and Scoping Trials, ESL-TR-87-03, Vol. 2 of 5, Air Force Engineering and Services Laboratory, Tyndall Air Force Base, Florida, April 1990.

9. Sheinson, R. S., "Halon Alternatives Extinguishment Pathways," Halon Alternatives Technical Working Conference, April 30-May 1, 1991, Albuquerque, NM, pp. 71-82.
10. Moore, T. A., Weitz, C. A., and Tapscott, R. E., "An Update on NMERI Cup-Burner Test Results," Halon Options Technical Working Conference, May 7-9, 1996, Albuquerque, NM, pp. 551-564.
11. Brabson, G. D., Walters, E. A., Schiro, J., Spencer, C., Tapscott, R. E., and Patterson, R. A., "The Role of the $\cdot\text{CF}_3$ Radical on Flame Extinguishment," Halon Options Technical Working Conference, May 7-9, 1996, Albuquerque, NM, pp. 611-613.
12. Sheinson, R. S., "The U. S. Navy Halon Total Flooding Replacement Program," in *Halon Replacements Technology and Science*, ACS Symposium Series 611, Miziolek, A. W., and Tsang, W., editors, (American Chemical Society, Washington, 1995), pp. 175-188.
13. Lias, S. G., Bartmess, J. E., Liebman, J. F., Holmes, J. L., Levin, R. D., and Mallard, W. G., "Gas-Phase Ion and Neutral Thermochemistry," *J. Chem. Phys. Ref. Data*, Vol. 17, suppl. 1, 1988
14. Takahashi, K., Inomata, T., Fukaya, H. and Abe, T., "New Halon Replacements Based on Perfluoroalkylamines: An Approach from the Other Side of Fluorine Chemistry," in *Halon Replacements Technology and Science*, ACS Symposium Series 611, Miziolek, A. W., and Tsang, W., editors, (American Chemical Society, Washington, 1995), pp. 139-150.
15. Grasselli, J. G., ed., *CRC Handbook of Physical Properties and Spectral Data for Organic Compounds* (CRC Press, Cleveland, 1973).