FLUORINATED ETHERS

A NEW FAMILY OF HALONS?

by

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ABSTRACT

Work in our laboratories to find suitable replacements for the fully halogenated CFC's and Halons has centered on the incorporation of oxygen as a heteroatom. The most stable class of compounds, the fluorinated ethers, potentially double the number of candidates versus just the halogenated alkanes, with minimal change in physical properties. Our first choice of compounds involves the dimethyl ether series of compounds which provide us with substitutionally similar analogues to the ethanes. Thus CF_3-O-CF_3 <=> CF_3CF_3; CF_3-O-CF_2Br <=> CF_3CF_2Br; $BrCF_2$-O-CF_2Br <=> $BrCF$ CF_2Br; HCF_2-O-CF_2Br <=> HCF_2CF Br and HCF_2-O-CF_2H <=> HCF_2CF_2H represent a series of substitutional analogues which though similar in physical properties are sufficiently different in chemical and physiological properties to represent a distinct class of compounds.

The synthesis, chemical characterization, physical properties measurement and extinguishment capabilities of this class of compounds will comprise the subject of this paper.

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Work in our laboratories to find suitable replacements for the fully halogenated CFC's and Halons has centered on the incorporation of oxygen as a heteroatom. The most stable class of compounds, the fluorinated ethers, potentially double the number of candidates versus just the halogenated alkanes, with minimal change in physical properties. Our first choice of compounds involves the dimethyl ether series of compounds which provide us with substitutionally similar analogues to the ethanes. Thus CF_3-O-CF_3 <=> CF_3CF_3; CF_3-O-CF_2Br <=> CF_3CF_2Br; $BrCF_2$-O-CF_2Br <=> $BrCF_2CF_2Br$; HCF_2-O-CF_2Br <=> HCF_2CF_2Br and HCF_2-O-CF_2H <=> HCF_2CF_2H represent a series of substitutional analogues which though similar in physical properties are sufficiently different in chemical and physiological properties to represent a distinct class of compounds.

The first challenge in investigating these compounds was in developing synthetic methods for their production. All of the above mentioned ethers can be prepared from the bromination of either pentafluorodimethyl ether **(E-125)** or tetrafluorodimethyl ether **(E-134)** which at one time were commercially available. They are no longer available. This has required that all the starting materials from this group had to be synthesized by aerosol direct fluorination of dimethyl ether with careful control of the fluorine/ether molar ratios. The reaction was carried out without the photochemical stage of the reactor activated.

SLIDE 1

SYNTHESIS OF FLUORINATED DIMETHYL ETHERS

Run No.	Total weight –	COMPOUNDS CF_3OCF_3	CF_3OCF_2H	CF_3OCFH_2	CF_2HOCF_2H	CF_2HOCFH_2
10	10.4	2.6	35.5	2.4	56.8	2.6
12	14.2	50.2	41.4		8.3	
13	11.5	93.7	6.3			

++ Product weighed after washing, 3.68 Grams of dimethyl ether was injected.

The aerosol fluorination is exceptionally efficient at producing these compounds as a mixture but relative to the almost trivial difficulty of producing perfluorinated materials, requires considerable optimization followed by non-trivial separations. Small quantities of material for characterization are easily separated by gas chromatography. The characterizations are shown on the following slides: **(2-6)**

SLIDE 2

CHARACTERIZATION OF E-116

F-DIMETHYL ETHER

CF_3-O-CF_3

^{19}F NMR: **-58.35** ppm, s.

FTIR (cm^{-1}): **2356.81(w), 2329.32(w), 1330.18(s), 1252.93(s), 1176.19(s), 1114.64(w), 969.50(m), 696.69(w), 667.34(w).**

SLIDE 3

CHARACTERIZATION OF E-I25

PENTAFLUORODIMETHYL ETHER

CF_3-O-CF_2H

a b c

^{19}F NMR: ϕ_a = **-58.79** ppm, t **(3)** J_{ab} = **4.45** Hz

ϕ_b = **-86.12** ppm, d-q **(2)** J_{bc} = **69.41** Hz

J_{ab} = **4.42** Hz

^1H NMR: δ = **6.14** ppm, t $J_{//}$ = **69.29** Hz

FTIR (cm^{-1}): 3027.53(w), **1368.95(w), 1302.82(s), 1225.41**(s), **1163.82**(s), **1118.34(s), 1029.62(w), 916.03(m), 731.55(m).**

SLIDE 4

CHARACTERIZATION OF E-134a

TRIFLUOROMETHYL FLUOROMETHYL ETHER

CF_3-O-CFH_2

a bc

^{19}F NMR: ϕ_a = -61.07 ppm, s (3)

ϕ_b = -155.73 ppm, t (1) J„ = 51.85 Hz

'H NMR: 6, = 5.16 ppm, d J„ = 51.72 Hz

FTIR: (cm^{-1}) 3029.48(w), 2952.31(w), 2841.12(w), 1504.09(w), 1434.97(w), 1288.35(s), 1239.51(s), 1201.68(s), 1161.97(m), 1104.17(m), 1064.39(s),851.34(w), 685.11(w),645.23(w), 601.76(w), 525.79(w).

SLIDE 5

CHARACTERIZATION OF E-I34

BISDIFLUOROMETHYL ETHER

CF_2H-O-CF_2H

a b a'b'

^{19}F NMR: ϕ_a = -85.52 ppm, d-t J_{ab} = 70.74 Hz $J_{aa'}$ = 3.87 Hz

^{1}H NMR: 6 = 6.12 ppm, t J_{ab} = 70.76 Hz

FTIR (cm^{-1}): 3046.21(w), 1380.12(m), 1361.19(m), 1196.15(s), 1138.87(s), 1086.13(s), 1010.63(m), 780.94(w), 730.35(w), 528.75(w).

SLIDE 6

CHARACTERIZATION OF E-143

DIFLUOROMETHYL FLUOROMETHYL ETHER

$CF_2H\text{-}O\text{-}CFH_2$

ab cd

^{19}F NMR:	ϕ_a = -85.96 ppm, d-d (2)	J_{ab} = 72.89 Hz
		J„ = 6.10 Hz
	ϕ_c = -155.80 ppm, t-t (1)	J„ = 52.31 Hz
		J„ = 6.03 Hz
H NMR:	δ_b = 5.93 ppm, t (1)	J_{ab} = 73.20 Hz
	δ_d = 5.07 ppm, d, (2)	J_{cd} = 52.70 Hz

FTIR (cm^{-1}): 3030.97(m), 2949.77(w), 1427.02(w), **1384.10(m),** 1356.81(w), **1287.15(m),** 1172.60(s), 1102.29(s), 1076.43(s), 1020.85(s), 972.90(w), 742.69(w), 689.75(w), 667.44(w).

^{19}F NMR Standard $CFCl_3$ as 0.0 ppm, (integral); ^{1}H NMR Standard TMS as 0.0 ppm, (integral); FTIR were measured in a gas cell at approximately 2 torr.

Production of the brominated analogues is conceptually very simple. Since elemental bromine will not substitute these ethers in good yields before decomposition occurs, we have employed the more reactive interhalogen compound, bromine chloride. Essentially equimolar amounts of chlorine and bromine form bromine chloride on short pre-irradiation of the halogen mixture prior to introduction of the fluorinated ether. A small excess of bromine suppresses virtually any chlorination, however, too large an excess significantly slows the rate of reaction. As can be seen in Slide 7, it is possible to get stepwise bromination of the dihydryl fluoroether, $HCF_2\text{-}O\text{-}CF_2H$, E-134.

SLIDE 7

SYNTHESES OF BROMINATED FLUORODIMETHYL ETHERS

1) $CF_3\text{-}O\text{-}CF_2H$ + BrCl -> $CF_3\text{-}O\text{-}CF_2Br$ t HCl

2) $HCF_2\text{-}O\text{-}CF_2H$ t BrCl -> $HCF_2\text{-}O\text{-}CF_2Br$ t HCl

3) $HCF_2\text{-}O\text{-}CF_2H$ + 2BrCl -> $BrCF_2\text{-}O\text{-}CF_2Br$ + 2HCl

The characterization of the three brominated products are given on the next three slides.

SLIDE 8

CHARACTERIZATION OF E-12581

BROMOPENTAFLUORODIMETHYL ETHER

$$\underset{a}{CF_2Br}\text{-}O\text{-}\underset{b}{CF_3}$$

^{19}F NMR: ϕ_a = -21.18 ppm, q (2), J_{ab} = 8.83 Hz
ϕ_b = -56.87 ppm, t (3), J = 8.85 Hz

FTIR (cm^{-1}): 1296.90(s), 1241.90(s), 1199.80(s), 1136.41(s), 1070.45(s), 904.70(m), 881.62(m), 830.73(w), 755.91(w), 720.45(w), 667.48(w), 633.50(w).

Anal. Calcd for C_2F_5BrO:	C, 11.18;	F, 44.20;	Br, 37.18.
Found:	C, 11.14;	F, 44.09;	Br, 36.87.

SLIDE 9

CHARACTERIZATION OF E-124B1

BROMODIFLUOROMETHYL DIFLUOROMETHYL ETHER

$CF_2Br\text{-}O\text{-}CF_2H$

a b

^{19}F NMR: ϕ_a = -19.55 ppm, t (2), J_{ab} = 3.66 Hz

ϕ_b = -86.88 ppm, d-t (2), J„ = 3.66 Hz, J_{bH} = 69.15 Hz

'H NMR: 6, = 6.31 ppm, t, J_{Hb} = 69.34 Hz

FTIR (cm^{-1}): 3024.86(w), 1398.84(m), 1366.60(m), 1240.98(s), 1186.30(s), 1152.62(s), 1131.85(s), 1106.68(s), 1041.84(s), 912.03(w), 838.90(w), 818.30(w), 779.46(s), 657.43(w), 564.40(w).

Anal. Calcd for C_2F_4HBrO: C, 12.20; H, 0.51; F, 38.59; Br, 40.58

Found: C, 12.33; H, 0.57; F, 38.38; Br, 40.86.

SLIDE 10

CHARACTERIZATION OF E-114B2

BISBROMODIFLUOROMETHYL ETHER

$CF_2Br\text{-}O\text{-}CF_2Br$

^{19}F NMR: ϕ = -19.91 ppm, s.

FTIR (cm^{-1}): 1229.89(s), 1180.64(s), 1119.29(s), 1095.42(s), 1028.19(s), 914.40(w), 835.34(m), 801.57(m), 741.90(m), 583.39(w).

Anal. Calcd for $C_2F_4Br_2O$: C, 8.71; F, 27.55; Br, 57.94.

Found: C, 8.89; F, 27.84; Br, 58.00.

We have additionally synthesized CF_2Br-O-CF_2Cl and HCF_2-O-CF_2Cl as side products in small quantities. Sufficient quantities of the first two brominated fluoroethers have been accumulated to determine physical properties: (Slide 11)

SLIDE 11

PHYSICAL PROPERTIES OF THE
BROMINATED FLUORODIMETHYL ETHERS

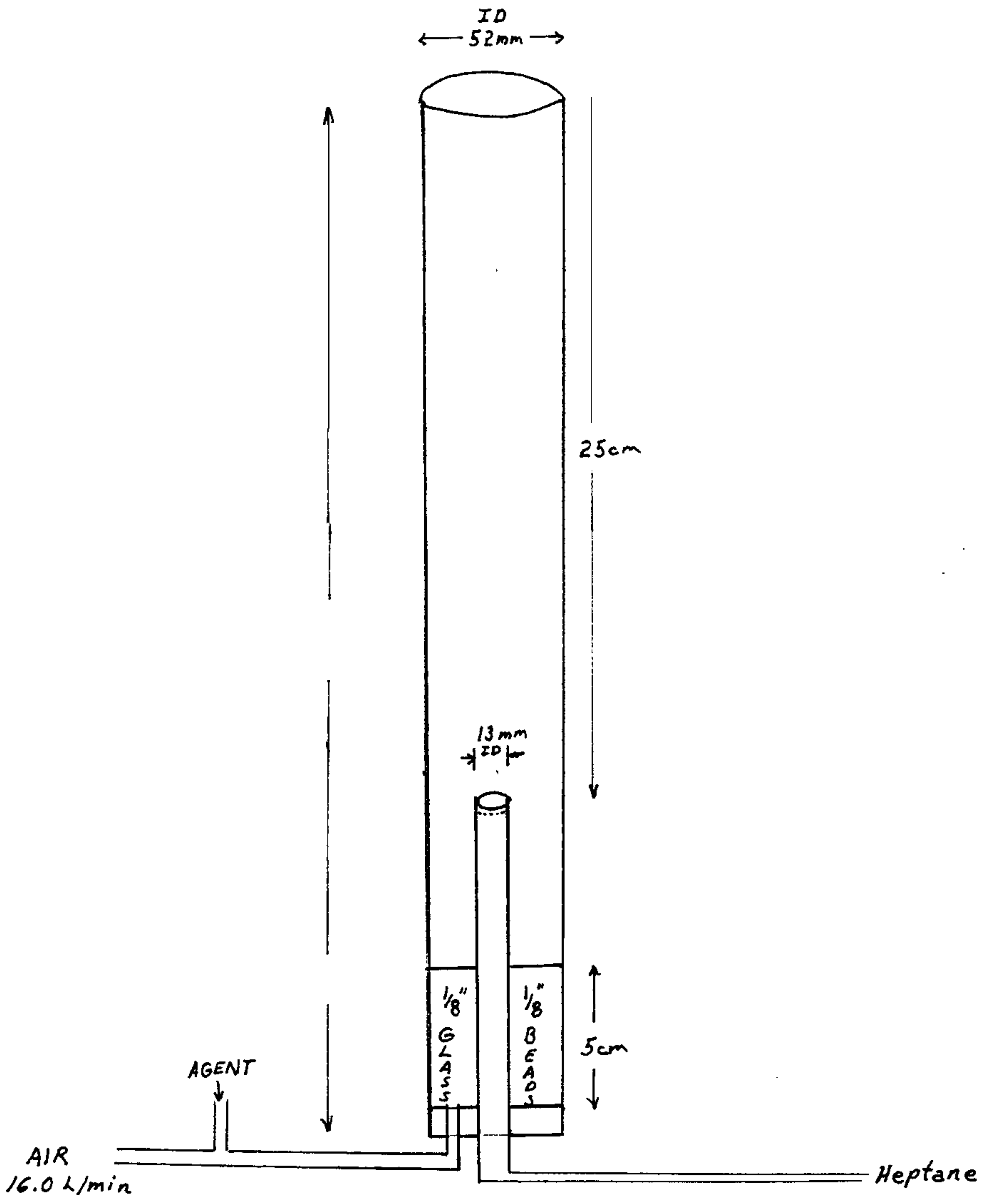
Compound	T_m	T_b	T_c	ΔH_{vap}
CF_3-O-CF_2Br	glass	-5.4°	+123.6°	23.51 kJ/mol
CF_3CF_2Br		-21°		
HCF_2-O-CF_2Br	glass	+24.6°	+172.6°	25.92 kJ/mol

However insufficient amounts have been produced to date to obtain cup-burner extinguishant concentrations. As a result we have turned our attention to perfluorinated ethers.

Perfluorinated ethers have zero ODP and unknown GWP due to uncertainty in their atmospheric lifetimes. We have sought in this, so far, limited study to understand the effect of the incorporation of oxygen into the perfluorocarbon chain on the effectiveness of the compound to function as an extinguishant. In order to carry out extinguishant studies a cup-burner patterned after the ICI model was constructed. It is very similar in size to the 5/8 scale unit constructed by Robert Tapscott's group at the NMERI Center for Global Environmental Technologies, and was based on the model constructed by Dr. Mark L. Robin at Great Lakes Chemical Corporation. (Slide 12)

SLIDE 12

THE TENNESSEE CUP-BURNER



Data obtained using this burner is very similar to data obtained by Tapscott and presented the Symposium on Progress in the Development and Use of CFC Alternatives, 200th National Meeting of the American Chemical Society, August 1990, Washington DC. Comparisons are shown in Slide 13.

SLIDE 13

COMPARISONS OF NMERI & TENNESSEE CUP-BURNER DATA

Compound	Extinguishant Concentration, V/V% Tennessee	 NMERI	BP, °C	T_c
CF_2Cl_2, R-12	7.8	--	-29.8'	112'
CF_2HCl, R-22	11.1	12	-41°	96'
CF_3H, R-23	12.6	12	-82'	25.9'
CF_2BrCl, R-1281[a]	3.5	3	-4'	..
CF_3Br, R-13B1[b]	2.7	3	-58°	67'

[a] Halon 1211, [b] Halon 1301

It is generally thought that Halons function chemically as well as physically in fire suppression. The chemical role is thought somehow to interfere in the propagation of free radical chains in the free-radical chain oxidation known as burning or fire. This chemical role has been most generally accepted for the bromine containing HALONS and the Hydrogen Bromide Flame Suppression Cycle shown in Slide 14 is thought most important.

SLIDE 14

HYDROGEN BROMIDE FLAME SUPPRESSION CYCLE

CF_3Br + H• -> CF_3• + HBr

HBr + H• -> H_2 t Br•

Br• t Br• t M -> Br, t M^*

Br_2 + H• -> HBr + Br•

A proposed trifluoromethyl radical suppression mechanism has been proposed by Tapscott and others.(Slide 15)

SLIDE 15

TRIFLUOROMETHYL SUPPRESSION MECHANISM

$$CF_3\bullet + HO\bullet \to CF_2O + HF$$

$$CF_2O + H\bullet \to HF + CFO$$

A passive mechanism has been proposed for heavier Halons having many degrees of vibrational freedom. (Slide 16)

SLIDE 16

THIRD BODY RADICAL SUPPRESSION MECHANISMS

$$H\bullet + H\bullet + M \to H_2 \text{ t } M^*$$

$$H\bullet + HO\bullet \text{ t } M \to H_2O + M^*$$

$$\bullet O\bullet + HO\bullet + M \to HOO\bullet + M^*$$

$$\bullet O\bullet \text{ t } H\bullet + M \to HO\bullet + M^*$$

There are literally hundreds of "hot-body" species in a rapidly propagating fire. These examples are only representative. This mechanism is principally a third-body, energy dissipative mechanism in which the halon collisionally deactivates excited state molecules, radicals or atoms. The constraint on this mechanism as depicted is the probability of three-body collisions. This mechanism may very well play an important role in damping the run-away chain kinetics found in spreading flames, especially if the "three-body'' collision may be effective for what is really a fast set of two, two-body collisions. The results of our tests on a few perfluorinated ether compounds as compared to selected perfluoroalkanes may shed some light on the importance of this mechanism in the suppression of flames.

Comparison of the flame extinguishant concentrations for F-cyclopropane and F-cyclobutane is informative in distinguishing whether radical formation by ring cleavage is a mechanism of fire suppression in perfluorocarbons. (Slide 17)

SLIDE 17

FLAME EXTINGUISHANT CONCENTRATIONS

CYCLIC PERFLUOROALKANES

Comoound	Extinquishant Concentration. V/V%	BP, °C
C-318, $(CF_2)_4$	$7\%^a$	-6'
C-216, $(CF_2)_3$	flammable	-31"

[a] NMERI

It is clearly seen that ring opening in the perfluorocyclopropane molecule contributes to its flammability, not *to* its extinguishant capability! This would indicate that carbon centered free radicals, even fluorocarbon free radicals, are fuel sources, not extinguishant attributes. It seems clear that the perfluorocyclobutane ring remains intact, at least in the low temperature diffusion flames provided by the cup-burner. Slide 18 shows the effect of replacing a $-CF_2-$ in a ring with -O-.

SLIDE 18

FLAME EXTINGUISHANT CONCENTRATIONS

CYCLIC PERFLUORINATED ALKANES VS ETHERS

Comoound	Extinquishant Concentration, V/V%	BP, °C
C-318, cy-$(CF_2)_4$	$7\%^a$	-6'
E-216, cy-$(CF_2)_3$-O-	8.5%	-28.4'

[a] NMERI

The major difference between F-oxetane, cyclo-$CF_2CF_2CF_2$-O-, and F-cyclobutane is two less C-F bonds, fewer degrees of freedom. The change of $-CF_2-$ by -O- has minimal effect on the ring stability due to the near equivalence of C-O and C-C bond dissociation energies. We clearly see here a reduction in the effectiveness of the

F-oxetane relative to the F-cyclobutane.

The effect of reducing the degrees of freedom by forming a ring is likewise effective in reducing the effectiveness of the extinguishant species. For example, Slide 19, shows that removing two terminal fluorine and connecting the carbon atoms has a noticeable effect on the extinguishant performance.

SLIDE 19

FLAME EXTINGUISHANT CONCENTRATIONS

ACYCLIC VS CYCLIC PERFLUOROETHERS

Compound	Extinwishant Concentration. V/V%	BP, °C
CF_3-O-CF_2-O-CF_3	6.9%	-9.7'
cy-CF_2-O-CF_2-O-CF_2-	7.5%	-22.1'

It can be clearly seen that bonds internal to the chain or ring have less effect on the extinguishant effectiveness than the number of terminal C-F bonds. In fact **it** seems that the most predictable measure of a non-brominated and non-chlorinated extinguishant molecules effectiveness is the number of C-F bonds in the molecule. The number of ether linkages in the chain has minimal effect on the effectiveness as can be seen in Slides 20 and 21.

SLIDE 20

FLAME EXTINGUISHANT CONCENTRATIONS

A CORRELATION WITH NUMBERS OF C-F BONDS

#C-F	Compound	Extinquishant Concentration, V/V%	BP, °C
6	cy-$CF_2CF_2CF_2$-O-	8.5%	-28.4'
6	CF_3CF_3, FC-116	8%[a]	-78"
6	cy-CF_2-O-CF_2-O-CF_2-	7.5%	-22.1'

[a] NMERI

SLIDE 21

FLAME EXTINGUISHANT CONCENTRATIONS

A CORRELATION WITH NUMBERS OF C-F BONDS

#C-F	Comoound	Extinauishant Concentration. V/V%	BP. °C
a	$cy\text{-}CF_2CF_2CF_2CF_2$	7%[a]	-6'
a	$CF_3\text{-}O\text{-}CF_2\text{-}O\text{-}CF_3$	6.9%	-9.7'
a	$CF_3\text{-}CF_2\text{-}CF_3$	6%[a]	-36'

[a] NMERI

In conclusion it seems clear that the mechanism by which perfluorocarbons achieve their flame extinguishment capability is rooted more in the ability to dissipate the energy of free radicals and permit their recombination; than it is by any bond dissociative or other purely chemical mechanism.

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