THE INVESTIGATION OF CHEMICALLY ACTIVE CANDIDATE HALON REPLACEMENTS

Adam Chattaway, Julian Grigg and David J. Spring
Kidde International, Mathisen Way, Colnbrook,
Slough, Berkshire, SL3 0HB, UNITED KINGDOM

1.0   INTRODUCTION

The physical and toxicological properties and extinguishing efficiency of Halons 1301 and 1211 are ideal for total-flooding and streaming applications. Since their production ceased at the end of 1993, many alternative fire suppressants have reached the market place. Currently, hydrofluorocarbons dominate the industrial and commercial markets, followed by hydrochlorofluorocarbon blends and inert gases. Aerospace and specialised uses, such as the Channel Tunnel trains, are still dependent upon recycled halon for space and weight efficiency reasons. An alternative fire suppressant is required for these applications.

A suitable replacement fire suppressant is required to have the following:

- a high extinguishing efficiency due to a chemical fire suppression mechanism
- an insignificant ozone depletion potential and acceptable global warming potential
- the correct physical properties (especially volatility) for total flooding or streaming applications
- acceptable toxicity at the required extinguishing concentration
- acceptable price and availability

The properties of several fire suppressants are given in Table 1

Table 1. Properties of Several Fire Suppressants.

	Halon 1301	Halon 1211	HFC-227ea	HFC-236fa	HFC-125
Extinguishing Conc. / volume%	3.3±0.5 [1]	3.6±0.3 [1]	6.4±0.3 [1]	5.6 [2]	9.0±0.5 [1]
Toxicity (NOAEL) / volume%	5.0 [3]	0.5 [4]	9.0 [3]	10.0 [3]	7.5 [3]
Estimated Atmospheric Lifetime / years [5]	65	20	41	250	36
Boiling Point / °C	-58	-4	-17	-2	-49
Vapour Pressure at 25°C / bar(a)	16.0	2.8	4.5	2.8	13.1

2.0   GENERAL STRATEGY

2.1   Chemical Activity Requirement
It is well established that fire suppressants capable of terminating the radical chain reactions that propagate combustion are the most efficient in mass terms. This chemical activity usually comes from bromine or iodine atoms in gaseous or liquid fire suppressants. Therefore, in order for a halon replacement agent to have as low a concentration requirement as the halon it replaces, the candidate molecules will have to include bromine or iodine in their structures. Other necessary structural features are a functional group that promotes atmospheric degradation, since acceptable environmental properties (i.e., ODP and GWP) are unlikely to be obtained for molecules with atmospheric lifetimes greater than about **3** months [6]. This functional group must not introduce toxicological complications and the whole molecule should contain sufficient fluorine atoms to render it nonflammable. In addition, the agent must possess sufficient volatility to allow its use in the intended application (*viz.* total flooding or streaming).

2.2   Bromine Versus Iodine
The chemical, environmental, and toxicological properties of iodine-containing molecules are dominated by the facile cleavage of the carbon-iodine bond. Relevant bond strengths are compared in Table 2. This cleavage causes rapid degradation of these molecules (e.g., CF_3I) in the troposphere by photolysis and therefore low atmospheric lifetimes. However, the weak carbon-iodine bond significantly increases the toxicity (compare CF_3I with CF_3Br). Carbon - fluorine, -chlorine and -bromine bonds are stronger and are not cleaved by photolysis in the troposphere. These molecules (e.g., CF_3Br) are sufficiently stable to reach the stratosphere where they are involved in ozone depletion. A further point is that bromine-containing molecules have lower molecular weights than their corresponding iodine-containing molecules. This has implications for the boiling points of any candidate molecules (Table **3).** The candidate molecules selected in this study therefore did not contain iodine, hut they will contain bromine and an organic moiety that causes them to be broken down in the troposphere.

Table **2.** Bond Strengths in kJ/mol of Various Atoms
to Carbon in Simple Organic Molecules.

X	H	F	Cl	Br	I
CH_3-X	439	452	356	293	238
CF_3-X	448	548	360	297	226

Table **3.** Relative Boiling Points in "C of Simple Bromine
and Iodine-Containing Molecules.

X	Br	I	Difference
CH_3-X	4	42	+ 38
CF_3-X	-58	-23	+ 35
CH_3CH_2-X	40	70	+ 30

2.3   Mechanisms of Atmospheric Breakdown

The key structural feature of any environmentally acceptable bromine-containing candidate **fire** suppressant is that which causes the molecule to break down in the troposphere. For most organic molecules, the principal degradation mechanism is that of reaction with hydroxyl radicals (*OH), which are naturally present in the atmosphere. There are two basic reactions with •OH radicals :

- hydrogen atom abstraction

$$X\text{-}H + *OH \longrightarrow \cdot X + H_2O \qquad \text{(slow)}$$

$$\cdot X \longrightarrow \longrightarrow \text{final products} \qquad \text{(fast)}$$
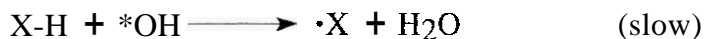
The rate of the whole process is controlled by the rate of the first reaction, the hydrogen abstraction reaction. The radical •X then breaks down very rapidly to the final products such as CO_2, H_2O, HF, HBr, etc., which are washed out of the atmosphere in rain. Clearly, the molecule must possess an abstractable hydrogen atom for this reaction to occur.

- addition to unsaturated molecules (alkenes and aromatics), e.g.,

$$\text{(slow)}$$

$$\text{finalproducts} \qquad \text{(fast)}$$

Furthermore, for molecules containing polar groups, there is also the possibility of wash out of the atmosphere with rain. However, such polar groups are likely to lead to enhanced toxicity and decreased volatility. Also, photodegradation is possible for molecules containing UV-absorbing chromophores.

For most molecules then, degradation in the atmosphere occurs through reaction with .OH radicals, and estimation of the lifetime of a molecule in the atmosphere, τ, comes to a measurement [7, 8] or calculation [7, 9] of the rate constant, k_{OH}, for reaction between the molecule and •OH since

$$\tau = \frac{4.9 \times 10^{-14}}{k_{OH}} \quad \text{years}$$

where k_{OH} is in units of cm^3 $molecule^{-1}$ s^{-1}. This equation assumes a global average •OH radical concentration of ⁻ 6.5×10^5 molecules cm^{-3} [10]. Note that some earlier texts (e.g., [7]) quote the •OH concentration as 1×10^6 molecule cm^3, thus there may be some variation in the precise form of the equation. Note also that to remove essentially all of a compound from the atmosphere requires three lifetimes. Since both ODP and GWP depend on the lifetime of a molecule in the atmosphere, it is desirable to have τ as short as possible, which means that in practise k_{OH} should be as large as possible. Although it is possible to measure k_{OH} for various

selected molecules [7, 8], structure-activity relationships are available [7, 9] to permit estimation of k_{OH} and hence τ [6].

However, the incorporation of these functional groups almost inevitably increases molecular weight and/or other intermolecular attractions, thereby decreasing agent volatility. This effect is examined in more detail in a subsequent paper [6].

3.0   AGENT SELECTION

3.1   Selection Rationale
Following the logic and guidelines in the previous section the choice of the tropospherically active moiety has to be a compromise between one that gives a high enough k_{OH} and one that does not compromise agent volatility too severely. After surveying all of the available options, two organic functional groups appeared to offer the best chance of achieving this goal—the methoxy group and the
the alkene group.

3.2   Agents Chosen
The ether, 2-bromo-1,1,2-trifluoro-1-methoxyethane (CH_3OCF_2CHFBr), was chosen for several reasons:

- probable high suppression efficiency (contains bromine and 71% halogen overall)
- low toxicity (this molecule has been previously studied [11-15] and was called Rofluorane® It was proposed **as** an anaesthetic in the early 1960s [16-20])
- short atmospheric lifetime (high k_{OH})
- ease of manufacture [15]
- probable acceptable volatility

Because propenes and butenes containing the —$CH=CH_2$ group were on the Advanced Agents Working Group (AAWG) list [21], a fully halogenated alkene, bromotrifluoroethene ($CF_2=CFBr$), was selected for the following reasons :

- probable very good fire suppression efficiency (contains bromine and 85% halogen overall)
- short atmospheric lifetime (high k_{OH})
- commercially available (50 g costs £1 12.00 from Fluorochem, Ltd.)
- acceptable volatility (gas at room temperature and pressure)

However, the toxicological profile of this molecule is not as good as that of the ether.
In addition to the above, we also examined hydrogen bromide (HBr) as an example of **an** inorganic bromine-containing molecule that (1) is volatile; (2) has a short atmospheric lifetime (it will be washed out of the atmosphere by rain, etc.); and **(3)** contains a very high % bromine by weight.

It should be emphasised that this was done purely on a scientific basis and not through any consideration that it would, in any way, make **a** practical agent (toxicity and corrosion considerations preclude this). Other inorganic species containing labile bromine atoms have

been studied previously, e.g., phosphorous tribromide (PBr_3) [22]. This latter compound suffers from the problem of being very involatile; it is solid over the lower part of the temperature range required by typical aviation specifications.

4.0 CANDIDATE MOLECULES

4.1 Preparation of 2-bromo-1,1,2-trifluoro-1-methoxyethane [15]

A stainless steel autoclave ($600 cm^3$) was charged with dry methanol ($130 cm^3$) and sodium (3 g). When hydrogen evolution had ceased bromotrifluoroethene (102 g, 0.63 moles) was added slowly (Reaction exothermic!). The transfer of bromotrifluoroethene was achieved by cooling the autoclave and therefore transferring the bromotrifluoroethene by distillation. The autoclave was then sealed and left to stand overnight. The vessel contents were then poured into distilled water ($800 cm^3$). The heavy organic layer was separated, washed with distilled water ($3x500 cm^3$), dried over anhydrous magnesium sulphate and distilled. 2-Bromo-1,1,2-trifluoro-1-methoxyethane (98 g, 80%, Bpt 85-89 "C) was obtained.

4.2 Physical Properties of the Candidate Molecules

Salient physical properties of the candidate molecules are given in Table **4.** Bromotrifluoroethene, a colourless gas at room temperature and pressure, boils at about –2 "C. 2-Bromo-1,1,2-trifluoro-1-methoxyethane is less volatile. It **is** a liquid at room temperature with a boiling point of 89 "C. HBr is very volatile with a boiling point of –87 "C.

Table 4. Data for the Selected Candidate Molecules

			HBr
CAS Number	679-90-3	598-73-2	10035-10-6
Mwt	192.96	160.92	80.91
Physical Form at 25°C / 1 atm	colourless liquid	colourless gas	colourless gas
Bpt / °C	89	-2	-87

The temperature dependence of the vapour pressure of $CF_2=CFBr$ and CH_3OCF_2CHFBr was determined in a glass pressure vessel, which was instrumented with a K-type thermocouple and a Kistler pressure transducer. The relationship of the vapour pressure with temperature for HBr has been measured previously [23]. The results are shown in Figure 1.

4.3 Toxicological Properties of the Candidate Molecules

The significant disadvantage of bromotrifluoroethene is its toxicity. **A** previous study reported that rats exposed to an initial concentration of 500 ppm for 4 hrs died [24]. However, the bromotrifluoroethene decomposed to carbonylbromofluoride and carbonylfluoride during the study. The actual concentration of bromotrifluoroethene was 5 to 10 ppm after 90 min of exposure. One of four rats died following exposure to an initial concentration of 279 ppm.
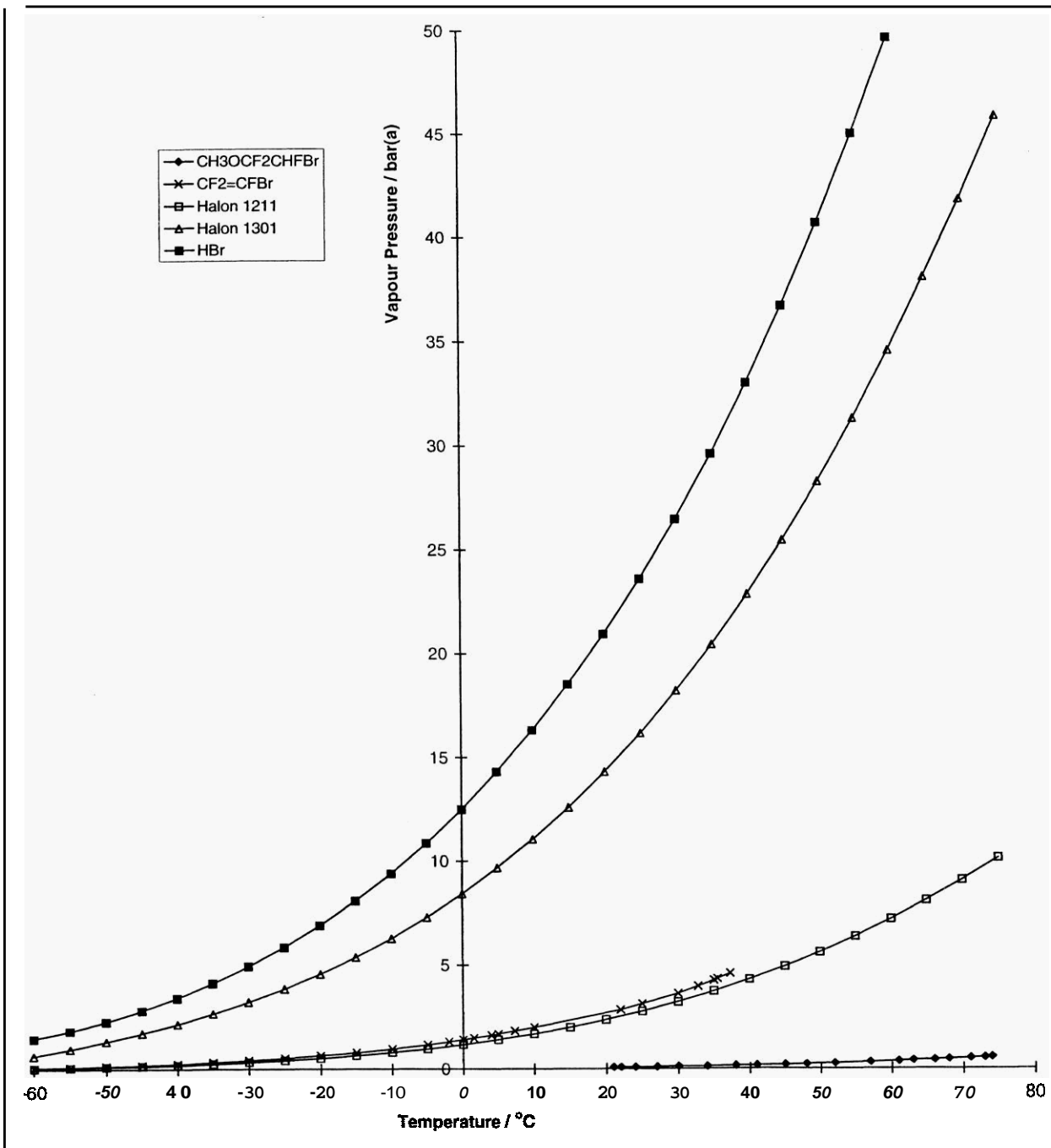
Figure 1. The dependence of vapour pressure on temperature for the candidate molecules.

The toxicology of 2-bromo-1,1,2-trifluoro-1-methoxyethane is much lower, as evidenced by the level of effort in evaluating it as an anaesthetic; the molecule proved an excellent anaesthetic at 2.5 volume% [19]. At this concentration it is not toxic. However, anaesthesia may clearly be a problem in any manned applications.

Hydrogen bromide has a high toxicity. The LC_{50} (inhalation, rats, 1 hr) is 2858 ppm [25].

5.0   ATMOSPHERIC LIFETIMES OF THE CANDIDATE MOLECULES

Using the structure-activity relationship method to estimate k_{OH}, as outlined by Atkinson [9] and also NIST [7], the k_{OH} for CH_3OCF_2CHFBr is estimated to be about 1.2×10^{-12} $cm^3molecule^{-1}s^{-1}$, which gives a lifetime, τ, of about 0.04 yrs (14 days). Other estimates by ICI have produced values of about 50 days [26].

For the alkene, $CF_2=CFBr$, the same methods produce an estimate of k_{OH} of about 4.3×10^{-13} $cm^3molecule^{-1}s^{-1}$, and an estimate for τ of 0.11 yrs (40 days). Please note that these methods of estimating k_{OH} are approximate, and the resultant values of τ should be used as guidelines only.

6.0   Fire Test Results

6.1   Test Apparatus
A diagram of the 195-L small-scale fire test chamber is given in Figure 2. The chamber could be sealed and was equipped with a transparent door for observation and access. The fire threat was heptane on water (70 mm diameter, heptane volume $30\,cm^3$). It was positioned in the centre of the base of the chamber underneath a steel baffle plate (dimensions 300 x 300 mm) to prevent direct impingement of the suppressant on the fire and to therefore examine total-flooding ability. The fire size to room volume parameter was $7.3\,kWm^{-3}$ [27].

Known masses of agents were contained in a 0.3-L pressure vessel at 23 ± 3 "C. In addition to $CF_2=CFBr$, CH_3OCF_2CHFBr, and HBr, HFC-227ea and Halon 1301 were used as reference agents. With HFC-227ea, $CF_2=CFBr$, and CH_3OCF_2CHFBr the vessel was superpressurised to 10 bar with nitrogen prior to discharge. The suppressant container was not superpressurised when Halon 1301 and HBr were tested because these agents have room temperature vapour pressures above 10 bar.

6.2   Test Procedure
In each test the fire was lit and allowed to bum under ventilated conditions with the door open and the exhaust fan running. Measurements of the oxygen concentration at the position of the fire indicated that the ventilation rate was sufficient to prevent significant oxygen depletion in the chamber. After **45** sec the fan was stopped and the doors sealed. The fire continued to bum for a further 15 sec, after which the agent was discharged through a BETE P.54 nozzle, which gave fine atomisation. The oxygen concentration was about 20.9 and 20.3 volume % at the end of the 45-sec ventilated prebum and at the beginning of the agent discharge, respectively. If the fire was allowed to bum in the sealed chamber it self-extinguished due to oxygen starvation after about 170 sec. The discharge time of the suppressant was monitored by measuring the pressure decrease in the cylinder and the temperature at the nozzle orifice. The time of extinguishment of the fire was measured using a rapid response K-type thermocouple in the flame. The weight of the suppressant cylinder was measured before and after discharge to give the mass discharged.

6.3   Interpretation of Results
The suppressants were evaluated by comparing the times taken to extinguish the fire after the beginning of the suppressant discharge, which are plotted against the mass of agent discharged in Figure 3. **As** the mass of suppressant was decreased, the fire was extinguished more slowly. When insufficient agent was used to effect rapid extinction of the fire, the fire was extinguished by a combination of the agent, the lack of oxygen and the build up of combustion products.
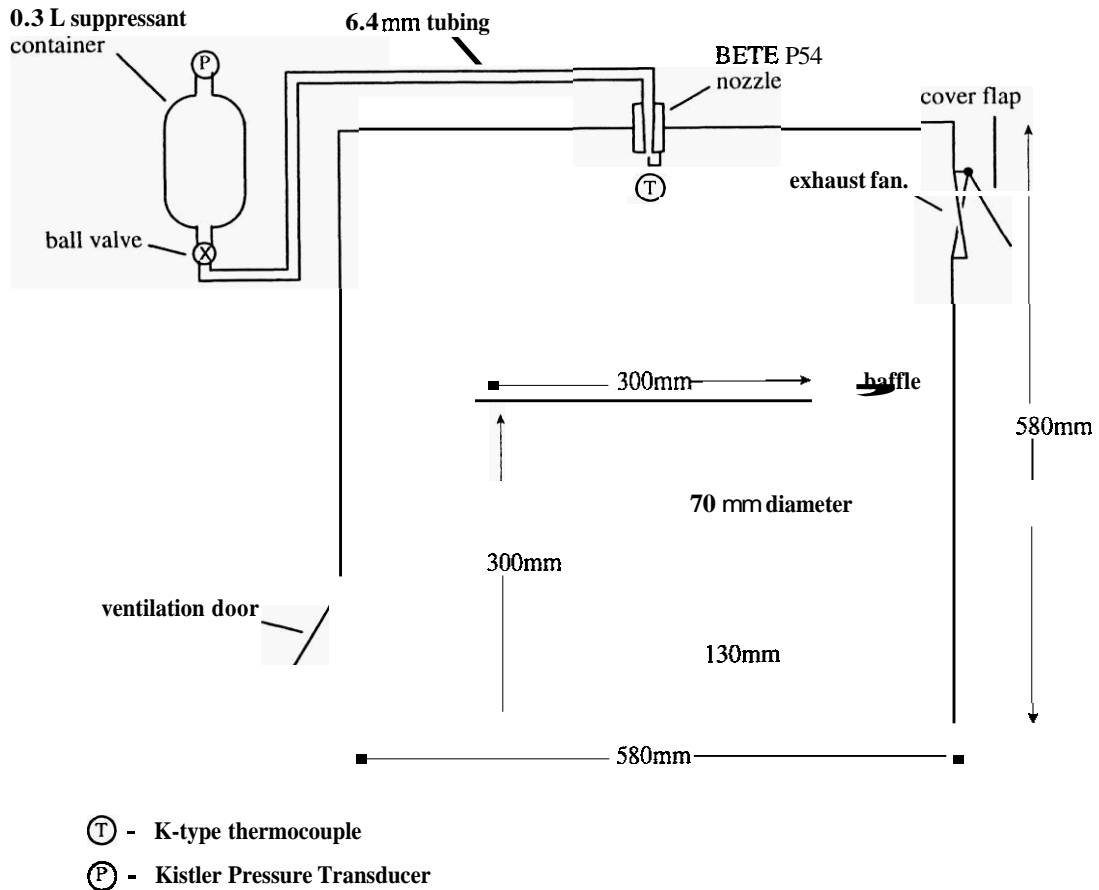
0.3 L suppressant container

6.4 mm tubing

BETE P54 nozzle

cover flap

exhaust fan.

ball valve

300mm → baffle

580mm

70 mm diameter

300mm

ventilation door

130mm

580mm

Ⓣ - K-type thermocouple

Ⓟ - Kistler Pressure Transducer

Figure *2*. The 195-L Test Chamber.

- Halon 1301
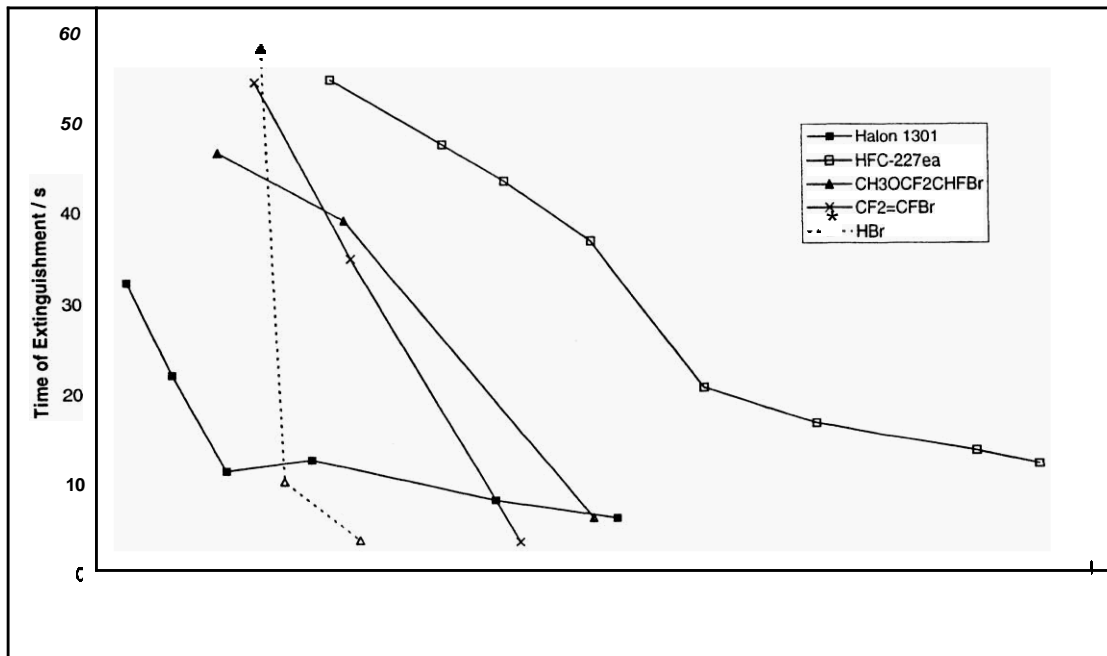- HFC-227ea
- CH3OCF2CHFBr
- CF2=CFBr
- HBr

Figure 3. The extinguishing efficiency of the candidate molecules.

Increased amounts of suppressant reduced the reliance on oxygen depletion and gave reduced extinguishment times. This trend continued until sufficient suppressant was discharged to extinguish the heptane fire unassisted by these other factors. Above this concentration the extinguishment time became largely invariant with the mass discharged.

7.0   DISCUSSION

7.1   Correlation of Measured Extinguishing Concentrations with Cup-burner Values
An estimation of the extinguishing concentration of a suppressant can be made from the data in Figure 3. Typically, the concentration values obtained using the 195-L test chamber in the current configuration were 1.0 to 1.3 times lower than literature values of the heptane cup-burner extinguishing concentration. This was due to factors such as agent concentration inhomogeneities (stratification), oxygen depletion, and the generation of combustion products by the fire, all of which reduce the suppressant concentration requirement relative to the cupburner concentration. Estimates of the extinguishing concentration for heptane for the candidate molecules are given in Table 5.

Agent	Mass Requirement in 195 L Chamber / g	Measured Extinguishing Conc. / volume%	Estimate of Heptane Cupburner Conc. /volume%
$CF_2=CFBr$	50	3.9	**4.5 ± 0.6**
CH_3OCF_2CHFBr	55	3.6	4.2 ± 0.6
HBr	35	5.4	*6.2 ± 0.8*

7.2   Extinguishing Concentration Versus Molecular Weight
For non-chemically acting agents, the extinguishing concentration is dependent upon the agent heat capacity [28] and therefore, to a first approximation, on the molecular weight (Figure 4).

Chemically acting agents are more efficient than would be predicted on the basis of their molecular weights. The measured extinguishing concentration for HBr is around 5.4 volume%. This is higher than for typical halons and may reflect the low molecular weight and therefore the low heat capacity contribution to suppression [28]. The two candidate agents, $CF_2=CFBr$ and CH_3OCF_2CHFBr, have an intermediate efficiency because the organic functional group, which imparts atmospheric degradation, also imparts flammable characteristics, and therefore impairs the suppression efficiency. **This will be true for any tropodegradable chemically acting halon replacement.**

The alkene $CF_2=CFBr$ is quoted as being flammable [25]. In general, this was not noted in our tests apart from one incident where a combustion-like reaction (with air) was noted during an attempted vapour pressure measurement.
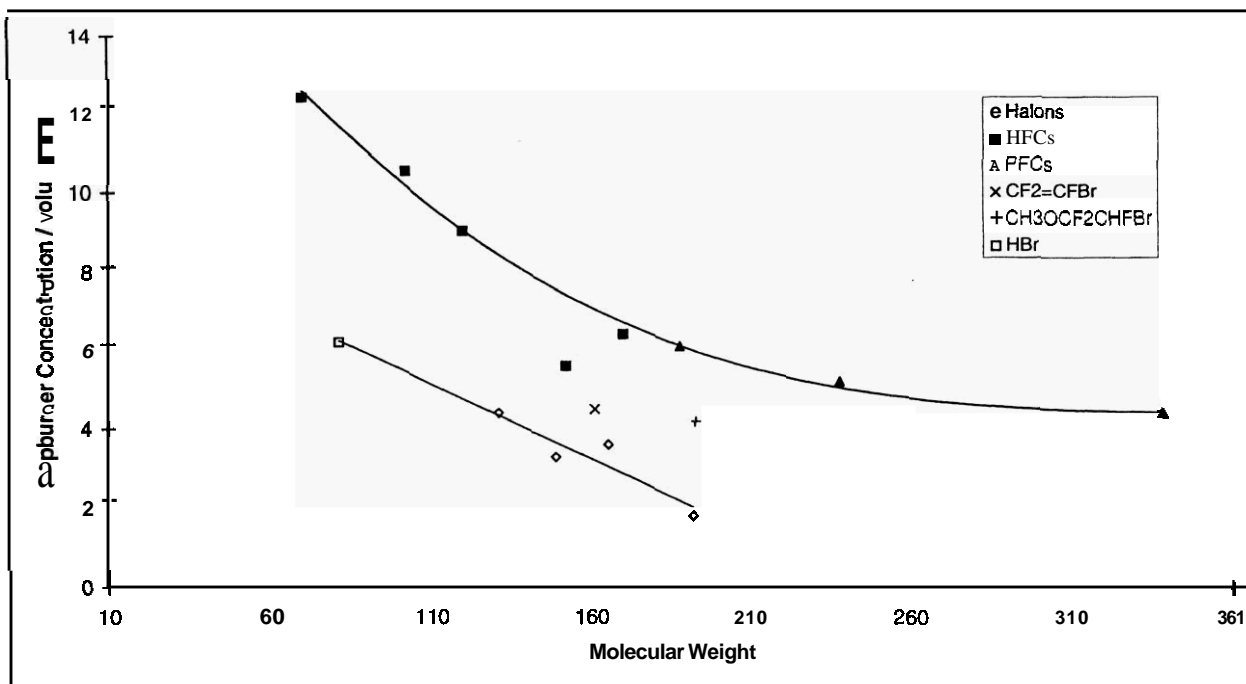
Figure **4.** The Variation of Extinguishing Concentration with Molecular Weight for Various Suppressants.

7.3 Volatility Implications of the Candidate Molecules

For a molecule to exhibit total-flooding fire suppression properties, its vapour **pressure** must equal or exceed the extinguishing concentration. Thus, on examining the vapour pressure/temperature characteristics for a given agent, it is possible to deduce a minimum temperature below which the molecule may not function effectively as a total flooding agent. Table **6** shows this for the candidate agents following a careful examination of Figure **1.** These considerations apply less stringently to streaming agents where system design means are used to deploy liquid agent directly into the flame.

Table 6. Suppression Properties of the Candidate Agents.

Agent	Estimated Cupburner Concentration / volume%	Minimum Temperature / °C	Vapour Pressure at the Minimum Temperature / bar(a)
CF$_2$=CFBr	4.5 ± 0.6	-70	0.045
CH$_3$OCF$_2$CHFBr	4.2 ± 0.6	6	0.042
HBr	6.2 ± 0.8	-107	0.062

8.0   SUMMARY

Three candidate halon replacement agents have been selected and tested as fire suppressants.

- $CF_2=CFBr$ has a measured extinguishing concentration of 3.9 volume% and may be considered as a total flooding agent above a temperature of $-70\,°C$. However, its high toxicity precludes use in normally occupied areas. Also, there are be question marks over the flammability of this material.
- CH_3OCF_2CHFBr has a measured extinguishing concentration of 3.6 volume% and may be considered as a total-flooding agent above 6 "C. It is, however, more toxicologically acceptable than the alkene.
- HBr has a measured extinguishing concentration of 5.4 volume%. It is sufficiently volatile to be considered as a total-flooding agent in any application above $-107\,°C$. However, it is much too toxic and reactive to be used in practise.

These results clearly illustrate the problems inherent in introducing tropodegradable groups into bromine-containing chemically acting suppressants. These arguments are pursued further in a companion paper at this conference [6].

9.0   REFERENCES

1.   Center for Global Environmental Technologies and New Mexico Engineering Research Institute, *Technical Update Series CGET5*, 1994, September 22.
2.   Moore, T.A., C. Weitz, and R.E. Tapscott. "An Update on NMERI Cup-Burner Test Results," in *Halon Options Technical Working Conference* 1996, Albuquerque, NM.
3.   Montreal Protocol Halon Technical Options Committee, "New Technology Fire Protection Alternatives for Fixed Halon Systems," *HTOC Technical Note #1* (971120), 1997.
4.   Halon Fire Extinguishing Agents Technical Options Committee (UNEP), *Montreal Protocol on Substances that Deplete The Ozone Layer*, 1994.
5.   World Meteorological Organisation, Global Ozone Research and Monitoring Project-Report No. 37, *Scientific Assessment of Ozone Depletion,* 1994.
6.   Ball, D.N., A. Chattaway, and D.J. Spring. "There Will be no 'Son of Supergas'," in *Halon Options Technical Working Conference* 1998, Albuquerque, NM.
7.   Gann, R.G., et al., *NIST Technical Note 1278,* 1990.
8.   Zhang, Z., et al., *J. Phys. Chem.,* 1994, **98**(16), p. 431.
9.   Atkinson, R., *Chem. Rev.,* 1986 **86,** p. 69.
10.   Wayne, R.P., *Chemistry of Atmospheres.* 1993, OUP. 234.
11.   Shainyan, B. and Z. Rappoport, *J. Org. Chem,* 1993 **58**(12), p. 3421-8.
12.   Jiang, X., G. Ji, and **Y.** Shi, *J. Fluorine Chem.,* 1987 **37**(3), p. 405-17.
13.   Lienert, E., Dtsch. Tieraerztl. Wochenschr., 1976 **83**(5), p. 198-203.
14.   Demiel, A., *J. Org. Chem,* 1960, **25**, p. 993-996.
15.   Spring, D.J., 1968: *Some Aspects of Fluorocarbanion Chemistry,* PhD Thesis, Department of Chemistry, University of Durham, NC.
16.   Russell, J.P., A.J. Szur, and R.C. Terrell, Patent, p. US 71-191811 711022.
17.   Terrell, R.C., Patent, p. FR 70-44177 701208.
18.   Terrell, R.C., Patent, p. US-68-712903 680314.
19.   Larsen, E.R., *Fluorine Chemistry Reviews,* 1969, **p.** 1-44.

20. Speers, L., A.J. **Szur,** and R.C. Terrell, *J. Med. Chem.,* 1972 **15**(6), p. 606-8.

21. Tapscott, R.E., et al. "Research on Advanced Agents as Halon Replacements." In *1996 International Conference on Ozone Protection Technologies.*

22. Haarland, P. *Labile Bromine-Containing Species as Fire Suppressants.* **In** *International Halon Replacement Working Group,* 1996, Heathrow.

23. Kaye, G.W.C. and T.H. Laby, *Tables of Physical and Chemical Constants,* 15th ed., 1986, London: Longman.

24. Kennedy, G.L., Crit. Rev. Tox., 1990 **21**(2), p. 149-70.

25. *CD-ROM Version of* **Sax's** *Dangerous Properties of Industrial Materials Eighth Edition,* ed. R.J. Lewis, 1994, London: **Van** Nostrand Reinhold.

26. McCulloch, A., ICI , Personal Communication, 1997.

27. Chattaway, A., J. Grigg, and D.J. Spring. "Halon Replacement Decomposition Product Studies." In *Halon Options Technical Working Conference* 1996, Albuquerque, NM.

28. Sheinson, R.S., J.E. Penner-Hahn, and D. Indritz, *Fire Safety Journal,* 1989 **15,** p. 437-450.