PHYSICAL AND ENVIRONMENTAL PROPERTIES
OF A NEXT GENERATION EXTINGUISHING AGENT

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Abstract

The issue of ozone depletion created great change for the fire protection industry. Research into environmentally acceptable compounds began with the search for materials that were less ozone depleting than halons. Early generations of replacements offered lower ozone depletion potentials but due to the inclusion of bromine and chlorine fell short of the goal of creating sustainable solutions. The search for acceptable alternatives advanced with the recognition that compounds with fluorine as the only halogen do not affect stratospheric ozone. The path to developing alternatives was long but industry eventually identified non-ozone depleting alternatives for virtually all of the uses of halons.

As difficult as the search for non-ozone depleting compounds had been, concerns over potential climate change have presented industry with even greater challenges. The search for low global warming potential compounds has progressed even more slowly. Viable next generation alternatives to halon need to be not only efficacious in fire extinguishing but also low in toxicity and possess sufficient chemical/thermal stability during handling and use. However, these properties are often at odds with the goal of creating materials with low global warming potentials. Normally, the stability and low toxicity provided via a high degree of fluorination also creates materials that can be long-lived in the atmosphere. To date, it appeared that the goals of creating compounds that are both atmospherically short-lived and safe to use were nearly mutually exclusive.

A novel class of compounds has been identified which combines these performance and environmental attributes. Fluoroketones are nonflammable and yet have surprisingly short atmospheric lifetimes and correspondingly low global warming potentials. Unlike previous fluorinated alternatives, fluoroketones photolyze readily in the atmosphere leading to atmospheric lifetimes on the order of days rather than years. In addition to these advantageous environmental properties these compounds have also exhibited acceptable toxicological profiles, allowing their use in a number of industrial applications, including fire protection. Use of a fluoroketone to replace high global warming potential compounds can virtually eliminate greenhouse gas emissions from those applications.

One fluoroketone in particular, referred to generically as C_6 F-ketone or FK-5-1-12mmy2 and commercially as 3M™ Novec™ 1230 Fire Protection Fluid, has performed well as a clean extinguishing agent in a variety of fire extinguishing tests and will have utility in numerous fire protection applications. As a result, this new agent looks to be a sustainable alternative to halons.

Introduction

Acceptable alternatives to halons require a complex combination of performance, safety and environmental properties. The halons had provided such useful physical and safety properties that they had created unique options to the fire protection engineer for fire suppression and inertion. Alternative compounds need to closely match these physical properties in order to be effective replacements. Applications employing halons and now their substitutes often result in some level of human exposure to the material. As a result, extensive toxicological testing is required to identify safe alternatives. Low toxicity alternatives are required in these applications in order to prevent increasing risk to the end-users.

Recognition of the adverse environmental impact of the halons and other ozone-depleting substances [1] has resulted in greater examination of the environmental properties of potential alternatives. Long-term alternatives must not deplete stratospheric ozone. Their atmospheric lifetimes need to be short enough to avert concerns over atmospheric accumulation and potential contribution to climate change. A short atmospheric lifetime is also necessary to minimize the global warming potential (GWP) of the compound [2].

This demanding combination of performance, safety and environmental properties is not easily found in organic compounds. Many chlorine and bromine containing compounds can be transported to the stratosphere where those halogens participate in the well-established catalytic ozone-depletion cycles [3]. Consequently, much of the early effort to develop alternatives has focused on fluorinated compounds: hydrofluorocarbons (HFCs) and to a lesser extent perfluorocarbons (PFCs). While these materials address some of the needs of a long-term alternative, concern has been raised that increased use of these materials may make a contribution to climate change or global warming [4].

All organic compounds that are emitted to the atmosphere have the potential to contribute to climate change i.e., act as greenhouse house gases. The potency of a greenhouse gas is a function of the infrared absorbance and atmospheric lifetime of the compound and expressed as a GWP.

The Global Warming Potential (GWP) is an index that provides a relative measure of the possible climate impact due to a compound, which acts as a greenhouse gas in the atmosphere. The GWP of a compound, as defined by the Intergovernmental Panel on Climate Change (IPCC) [2], is calculated as the integrated radiative forcing due to the release of 1 kilogram of that compound relative to the warming due to 1 kilogram of CO_2 over a specified period of time (the integration time horizon (ITH)):

$$GWP_x = \frac{\int_0^{ITH} F_x C_{xo} \exp(-t / \tau_x)\, dt}{\int_0^{ITH} F_{CO_2} C_{CO_2}(t)\, dt}$$

where F is the radiative forcing per unit mass of a compound (the change in the flux of radiation through the atmosphere due to the IR absorbance of that compound), C is the atmospheric concentration of a compound, τ is the atmospheric lifetime of a compound, t is time and x is the compound of interest.

The commonly accepted ITH is 100 years representing a compromise between short-term effects (20 years) and longer-term effects (500 years or longer). The concentration of an organic compound, x, in the atmosphere is assumed to follow pseudo first order kinetics (i.e., exponential decay). The concentration of CO_2 over that same time interval incorporates a more complex model for the exchange and removal of CO_2 from the atmosphere (the Bern carbon cycle model).

There are only two independent variables in the GWP calculation that are affected by the physical/environmental characteristics of the compound - the radiative forcing and the atmospheric lifetime. HFCs and PFCs absorb IR energy in the "window" at 8 to 12 μm which is largely transparent in the natural atmosphere. Absorption of IR energy within this atmospheric window is characteristic of all fluorinated compounds. As shown in Figure 1, the radiative forcing values for PFCs and HFCs scale essentially linearly with the number of carbon-fluorine bonds due to the specific IR absorbance of those bonds at nominally 8 μm (1250 cm^{-1}). This IR absorbance, coupled with their relatively long atmospheric lifetimes, makes HFCs and PFCs greenhouse gases with high GWPs. Since all fluorinated compounds will absorb IR in these wavelengths, the most effective approach to producing low GWP alternatives is to develop compounds with shorter atmospheric lifetimes.

Figure 1
Radiative Forcing of HFCs and PFCs
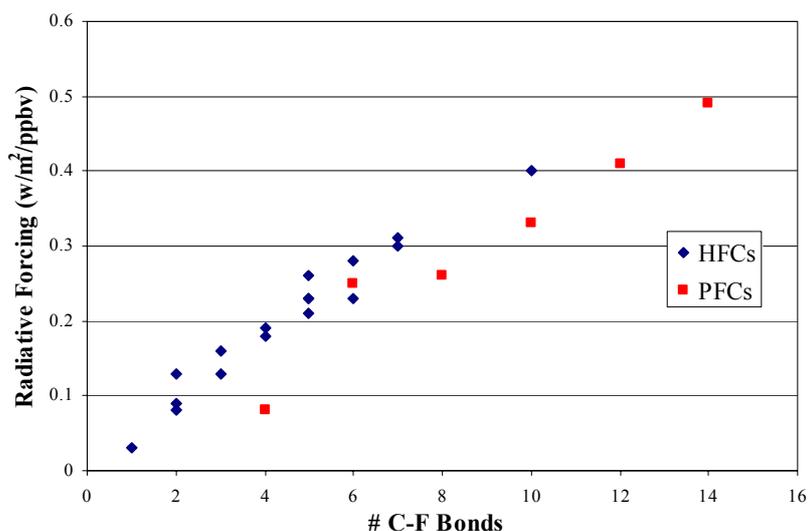
Data taken from reference 2.

Compounds with Short Atmospheric Lifetimes

Once emitted, there are a number ways for organic compounds to be removed from the atmosphere.

Rainout: Compounds with measurable water solubility can be removed from the atmosphere via rain out or wet deposition. However, the necessity of a clean extinguishing agent to contain a sufficient number of halogen atoms results in compounds with extremely low water

solubility, typically on the order of parts per million by weight. Compounds with such low water solubility are not effectively removed from the atmosphere via wet deposition or rainout

Oxidation: It has long been recognized that incorporation of hydrogen atoms into a fully halogenated molecule results in shorter lifetimes due to reaction with tropospheric OH radicals [5].   This characteristic was used advantageously in the development of first generation halon replacements. There is however a practical limit to the use of this approach to further reduce the atmospheric lifetime of halogenated alkanes. Adding hydrogen atoms to a molecule will decrease its lifetime but eventually will lead to the formation of a flammable compound. Compounds in which the number of carbon-fluorine bonds is less than the sum of the carbon-carbon and carbon-hydrogen bonds are typically flammable, rendering them useless for fire protection applications. In most classes of compounds, the incorporation of additional hydrogen atoms at the expense of fluorine atoms will lead to a flammable compound prior to producing a sufficiently short atmospheric lifetime. This is illustrated Table 1 and Figure 2 with the comparison of partially fluorinated ethanes.

Figure 2
Atmospheric Lifetimes Partially Fluorinated Ethanes
as Function of the Number of Carbon-Hydrogen Bonds
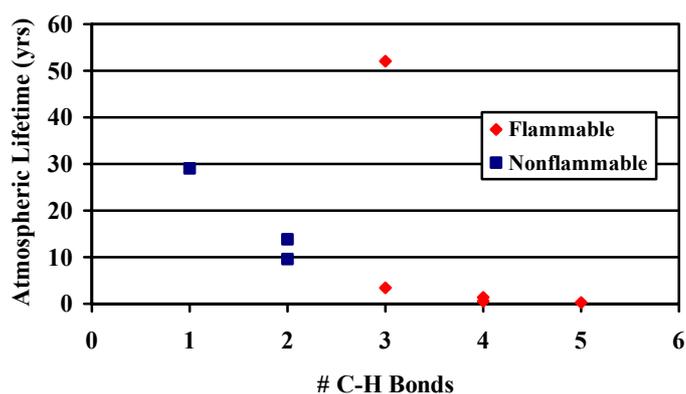
*Data taken from reference 2.

Table 1
Atmospheric Lifetimes and GWPs of Partially Fluorinated Ethanes

Compound	Halocarbon Number	Flammable	Atm. Lifetime (yrs) [2]	GWP [2] (100 Yr ITH)
CH_3CH_2F	HFC-161	Y	0.3	12
CH_3CHF_2	HFC-152a	Y	1.4	120
CHF_2CH_2F	HFC-143	Y	3.4	330
CH_3CF_3	HFC-143a	Y	52	4,300
CHF_2CHF_2	HFC-134	N	9.6	1,100
CH_2FCF_3	HFC-134a	N	13.8	1,300
CHF_2CF_3	HFC-125	N	29	3,400

<u>Photolysis</u>: Many compounds in the atmosphere decompose upon absorption of certain wavelengths of sunlight. This photolysis process varies with altitude due to the change in the wavelengths of light which penetrate the atmosphere. Only longer wavelength (lower energy) light penetrates into the lower atmosphere due to the absorbance of the shorter wavelengths of light (higher energy) by the natural atmosphere. As a result, compounds that require shorter wavelengths of light for decomposition will travel to much higher altitudes for photolysis to occur. The halons were subject to photolysis at short enough wavelengths (200-220 nm) that they were transported into the stratosphere (10-50 km) prior to decomposition, resulting in atmospheric lifetimes on the order of decades. In order to develop a material with a much shorter atmospheric lifetime, the compound will need to absorb energy at much longer wavelengths – in the near ultraviolet (UV).

One class of organic compounds with significant absorbance in the near UV is that containing a carbonyl group (C=O) such as aldehydes and ketones. Common ketones, such as acetone, have peak UV absorption around 280 nm. However, the fluorinated analogues of these ketones exhibit a bathochromic shift in absorbance (i.e., a shift in absorbance to higher wavelengths). Many fluoroketones demonstrate strong UV absorption with a maximum absorbance just above 300 nm as shown in Table 2.

Table 2
UV Absorption of Fluorinated Ketones

Compound	Peak UV Absorption (nm)
$CF_3C(O)CF_3$	302
$CF_3CF_2C(O)CF(CF_3)_2$	306
$CF_3CF_2CF_2C(O)CF(CF_3)_2$	305
$(CF_3)_2CFC(O)CF(CF_3)_2$	302
$CF_3CF_2CF_2C(O)CF(CF_3)_2$	307

The strong absorption in the near UV results in very short atmospheric lifetimes for these compounds. The compound which has been studied most extensively is $CF_3CF_2C(O)CF(CF_3)_2$. This material was recently commercialized as a clean extinguishing agent and is identified as FK-5-1-12mmy2 following an extension of the fluorochemical numbering system.

Environmental Properties of FK-5-1-12mmy2

A study conducted by MIT [6] examined the atmospheric loss mechanisms for FK-5-1-12mmy2. The authors of this study determined that this compound does not react with hydroxyl radical (OH) but that substantial decay occurs when exposed to UV radiation. The authors measured the UV cross-section for FK-5-1-12mmy2 finding a maximum wavelength of absorbance at 306 nm. Since this compound shows significant absorbance at wavelengths above 300 nm, photolysis in the lower atmosphere will be a significant sink for this compound. The authors conclude, "In fact, the absorption spectrum is similar to that of

acetaldehyde [7], a species whose lifetime against solar photolysis is about 5 days [8]. The absorption cross sections of L-15566 (the experimental product number for FK-5-1-12mmy2) are somewhat larger; hence, we expect the atmospheric lifetime of L-15566 against solar radiation to be of the order of 3 to 5 days". Recent laboratory measurements of the photodissociation rate of L-15566 found it to be equivalent to that for acetaldehyde, within experimental error [9]. Hence, an atmospheric lifetime of 5 days is appropriate for FK-5-1-12mmy2

The potential for FK-5-1-12mmy2 to impact the radiative balance in the atmosphere (i.e., climate change) is limited by its very short atmospheric lifetime and low global warming potential (GWP). Using a measured IR cross-section and the method of Pinnock et al. [10] the instantaneous radiative forcing for FK-5-1-12mmy2 is calculated to be 0.50 $Wm^{-2}ppbv^{-1}$. This radiative forcing and a 5 day atmospheric lifetime results in a GWP value of 1 using the WMO 1999 method and a 100 year integration time horizon. Clearly, compounds with such short atmospheric lifetimes are of no concern with respect to potential climate change.

FK-5-1-12mmy2 is expected to rapidly degrade to fluorinated alkyl radicals similar to those produced by other fluorochemicals. Studies of the atmospheric chemistry of these radical species and their degradation products have concluded that they have no impact on stratospheric ozone [11]. This, combined with its very short atmospheric lifetime, leads to the conclusion that FK-5-1-12mmy2, like other fluorinated compounds, has an ozone depletion potential of zero.

A summary of the environmental properties of FK-5-1-12mmy2 in comparison to halons and their first generation replacements appears in Table 3.

Table 3
Comparison of Environmental Properties of Fluoroketones
with halons and First Generation Alternatives*

Halocarbon No.	FK-5-1-12mmy2	halon 1301	HFC-227ea	HFC-236fa
Chemical Formula	$C_2F_5C(O)CF(CF_3)_2$	CF_3Br	CF_2CFHCF_3	$CF_3CH_2CF_3$
Atm. Lifetime (years)	0.014	65	33	220
Global Warming Potential (100 yr ITH)	1	6900	3500	9400
Ozone Depletion Potential (CFC-11 = 1)	0	10	0	0

* Data taken from reference 2 except for the new compound FK-5-1-12mmy2.

Thermo-physical Properties of FK-5-1-12mmy2

The physical properties of FK-5-1-12mmy2 are shown in Table 4. The properties of this material are similar to many of the first generation halon alternatives with one primary exception – this compound is a liquid at ambient conditions. The normal boiling point of FK-

5-1-12mmy2 is 49°C, meaning this compound has a much lower vapor pressure than the conventional clean agents, which are gases at ambient conditions. However, since FK-5-1-12mmy2 has the very low heat of vaporization characteristic of many fluorochemicals, this liquid is readily vaporized to form a stable concentration of vapor in air. At 25°C, one could form vapor concentrations up to 39 volume percent prior to reaching saturation.

Table 4
Properties of FK-5-1-12mmy2

Property	Unit	Value	Data Source
Molecular Weight		316.05	
Boiling Point	°C	49.0	from vapor pressure measurements
Freezing Point	°C	-108	measured value
Critical Temperature	°C	168.66	measured value
Critical Pressure	kPa	1865	measured value
Critical Volume	cc/mole	494.5	calculated from $V_c = Z_c R T_c / P_c$
Critical Density	kg/m^3	639.1	calculated from V_c
Specific Heat, Liquid @ 25°C	kJ/kg°C	1.1030	measured value
Specific Heat, vapor @ constant P (1atm & 25°C)	kJ/kg°C	0.891	measured value
Heat of vaporization @ bp	kJ/kg	88.0	measured value
Thermal Conductivity of liquid @ 25°C	W/m°C	0.0588	measured value
Viscosity, liquid @ 25°C	cp	0.524	measured value
Solubility of water in agent @ 21°C	wt%	<0.001	based upon detection limits
Vapor Pressure @ 25°C	kPa	40.36	measured value

The thermodynamic and transport properties have been measured for FK-5-1-12mmy2. The measured properties were used to develop a thermodynamic model for FK-5-1-12mmy2 using the PRSV (Peng-Robinson-Stryjek-Vera) equation of state

$$P = RT/(V - b) - a\alpha/[V(V + b) + b(V - b)]$$

where $a = 0.457235(RT_c)^2/P_c$
$b = 0.077796 RT_c/P_c$
$\alpha = \kappa_o + \kappa_1(1 + T_r^{0.5})(0.7 - T_r)$
$\kappa_o = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3$
$T_r = T/T_c$

The constants used in the PRSV Equation of State for FK-5-1-12mmy2 are shown in Table 5.

Table 5
Constants for PRSV Equation of State for FK-5-1-12mmy2

Molecular Weight	T_c, K	P_c, bars	Z_c	Acentric Factor, ω	κ_1
316.046	441.81	18.646	0.251	0.471	0.052

Like other highly fluorinated compounds, FK-5-1-12mmy2 exhibits a degree of departure from ideal gas behavior as indicated by the PRSV equation of state. An effect of this is a lower specific volume (or higher density) of the vapor than would have been predicted by the ideal gas law. A comparison of the ideal versus measured specific volumes appears in Figure 3. Engineering calculations need to employ these measured properties since the vapor density can differ from that calculated by the ideal gas law by several percent.

Figure 3
Ideal vs. Measured Specific Vapor Volume of FK-5-1-12mmy2
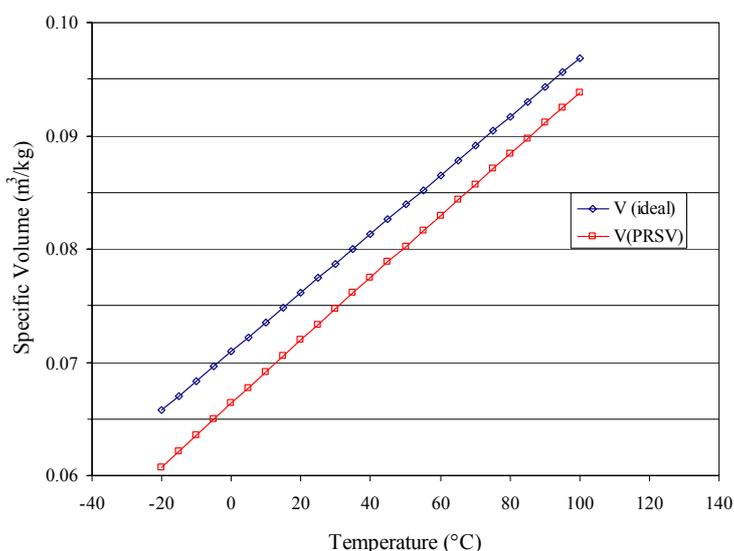
Conclusions

Fluoroketones are a useful class of compounds capable of providing molecules that are both nonflammable and atmospherically short lived. The very short atmospheric lifetimes result in low GWPs for these compounds. These environmental properties are distinctly different from those of the halons and their first generation replacements such as HFCs and PFCs.

The physical, transport and thermodynamic properties of a fluoroketone, FK-5-1-12mmy2, have been measured. These properties are being used in system and software development for use of this compound as a streaming agent and flooding agent in fire extinguishing applications. This combination of physical and environmental properties makes a compound such as FK-5-1-12mmy2 a sustainable alternative to halons in fire protection.

References

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