A-2.3 Development of Halon Replacements and Their Evaluation as Fire Extinguishers

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Abstract This program consists of the evaluation of the fire extinguishing ability and the investigation of fire extinguishing mechanism of polyfluoroamines. It was found that polyfluoroamines, which do not contain a bromine atom as the requisite atom for imparting high fire extinguishing ability, showed good fire extinguishing ability. Furthermore, comparative study on the laminar flame speed of methane and heptane flames for several polyfluoroalkylamines showed that perfluoro(N,N-dimethylethylamine) was more effective in fire extinguishing ability than perfluoro(triethylamine), which can not be explained by usual physical fire supression mechanism. For the explanation of this results, special action of CF_3-radical generated from the former compound on the fire suppression mechanism was considered. By studying the computational chemistry in terms of the action of CF_3-radical in fire, new fire-suppresion mechanism by CF_3-radical was found, of which CF_3-radical behaves catalytically as a radical scavenger for hydrogen and hydroxyl radicals in flame just like the role by a bromine radical generated from Halons.

Key Words Halon alternatives, Fire extinguisher, perfluoroamine, laminar flame speed, CF_3 radical, Fire supression mechanism

1. Introduction

The destruction of ozone layer has become the most urgent global environmental problem which should be resolved by international cooperation.[1] The phase-out of CFCs and Halons by the end of 1999 has been decided at the international meeting (London, 1990). However, the fact that the ozone layer is being destroyed far faster than scientists expected has called for the development of their alternatives and advanced the date of the phase out time of Halons and CFCs by the end of 1993 and 1995 respectively (Copenhagen, 1992).

2. Research Objective

This project aims at the development of polyfluoroamine-type Halons (degradable Halons) as the new Halon replacements. Halon replacements are required to have the less environmental impacts and low toxicities yet retaining the comparable fire extinguishing ability to that of the current non-degradable Halons.

The incorporation of the nitrogen atom in the perfluoroalkyl group of hard-Halons is considered to clear this propositions due to having some degradability at the C-F bond alpha to the nitrogen, and very low toxicity toward human body as their derivatives are being used as an artificial blood

3. Research Method

Our new Halon replacements program consists of the preparation of the derivatives of perfluoroamines, the evaluation of degradability and fire-extinguishing ability for these compounds. In order to get insight into the secret of high fire extingushing ability of polufluoroalkylamines, especially those containing a $(CF_3)_2N$- group, *ab initio* molecular orbital calculations were conducted for various reactions of $(CF_3)_2N$- in the combustion zone.

(1) Preparation of new Halon substitutes

Perfluoroalkylamines and their derivatives used in this experiments were all made by means of electrochemical fluorination[2]. Perfluorotrimethylamin, perfluoro(N,N-dimethylethylamine)

and perfluorotriethylamine were prepared by the electrochemical fluorination[3] of corresponding amines. Perfluoro(N,N-dimethyl-2-bromoethylamine)[4], perfluoro(N,N-dimethylvinylamine)[5], N,N-bis(trifluoromethyl)-1,1,2,2-tetrafluoroethylamine[6] were synthesized *via* consecutive several steps starting from perfluoro(3-dimethylamino-propionyl fluoride)[7]. The physical properties of these compounds are shown in Table 1.

Table 1. Properties of polyfluoroamines

Sample	bp (°C)	n_D^{20}	d_4^{20}
$(CF_3)_3N$	-10		
$(CF_3)_2NC_2F_5$	20~22		
$(CF_3)_2NCF_2Br$	40.6		
$(CF_3)_2NCF_2CF_2Br$	59.5~60.5	1.2963	1.8932
$(CF_3)_2NCF_2CF_2H$	32.0 (extraporated)		
$(CF_3)_2NCF=CF_2$	13.7 (extraporated)		
$(C_2F_5)_3N$	70.3	1.262	1.736

(2) Evaluation of fire extinguishing ability

The evaluation of fire extinguishing ability for these compounds was done by a box method (A) and also by measuring the burning velocities (laminar flame speed) of methane and heptane flames (B). Halon 1301 (CF_3Br), CO_2, carbon tetrachloride and 1,1,1,2,3,3,3-heptafluoropropane (FM200; Great Lakes) were also investigated for a comparison. The first method (A) provided the data concerning the relationship between the time required for extingushing flame in the box (20cm X 20cm X 20cm) and the concentration of additives. The second method (B) showed the inhibition effect on the burning velocities of the additives, of which order is comparable to that of the fire extinguishing ability. The determination of the delay of the ignition time behind a shock wave[8] was also carried out in order to clarify the behavior of polyfuoroalkylamines at the initial stage of the combustion.

4. Result

The results obtained by a box method are shown in Figure 1. Thus, following order of the fire extinguishing ability (reverse order of the extinguishing time) was observed for perfluoro-(N,N-dimethylamino-2-bromoethylamine), perfluorotriethylamine, Halon 1301, CO_2, and carbon tetrachloride: $CO_2 < CCl_4 < CF_3Br$, $(C_2F_5)_3N < (CF_3)_2NCF_2CF_2Br$

It was found that perfluorotriethylamine which have not a bromine atom in the molecule showed comparable fire extinguishing ability to that of Halon 1301.

Table 2 shows the data of burning velocities of methane and heptane flames with polyfluoroalkylamines. From these experiments, it was found that polyfluoroalkylamines had good inhibition effect on the burning. Among polyfluoroalkylamines, perfluoro(N,N-diemthylethylamine) and perfluorotrimethylamine showed unexpectedly better fire extinguishing ability than that of perfluorotriethylamine. And its inhibition effect was almost comparable to that of Halon 1301. Usually, better fire extingushing ability is expected for the compounds having higher molecular weight due to the increased action of physical fire supression mecanism in fire. From the measurement of the delay of the ignition time behind the shock wave[8] for polyfluoroalkylamines, it was clarified that the C-N bond of polyfluoroamines was very easy to cleave to yield polyfluoroalkyl radicals just on the beginning of burning.

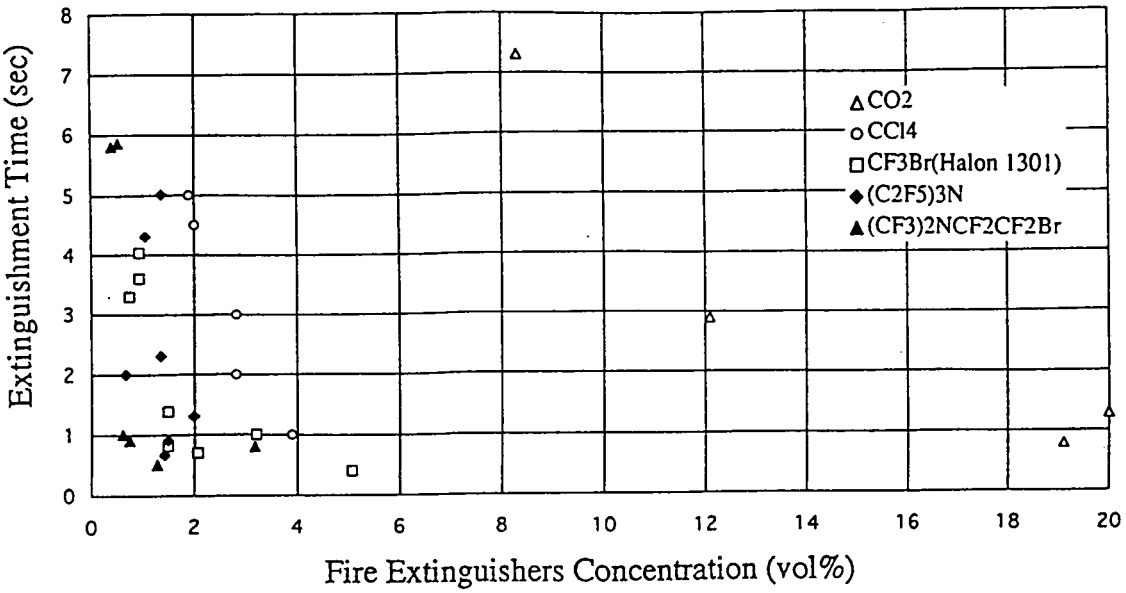

Figure 1. *Evaluation of fire extingushing ability of perfluoro(N,N-dimethyl-2-bromoethylamine) and perfluoro(N,N-dimethylethylamine)*

Table 2. *Burning velocities (Laminar flame speed) of methane and heptane flames*

Inhibitor	Methane flame [a]		Heptane flame [b]	
	Observed / $cm.s^{-1}$	Decreasing ratio / %	Observed / $cm.s^{-1}$	Decreasing ratio / %
none	38.6		44.5	
CO_2	38.4	0.5	41.1	7.6
CF_3Br	22.9	41	30.4	32
CF_3CFHCF_3	33.7	13	38.0	15
$(C_2F_5)_3N$	28.2	27		
$(CF_3)_2NC_2F_5$	27.7	28	32.6	27
$(CF_3)_2NC_2F_4H$	29.4	24	33.2	25
$(CF_3)_2NCF=CF_2$	28.8	25	34.2	23
$(CF_3)_3N$	27.6	28	33.2	25

a) Methane flame : 9.5%CH4 + 0.5%Additive + 90.0%Air

b) Heptane flame : 1.87%C_7H_{16} + 0.5%inhibitor + 97.63%Air

5. Discussion

Halons function chemically as well as physically in fire suppression. High effectiveness in fire suppression by Halons is primarily based on the chemical suppression mechanism due to the presence of a bromine atom. However, the fact that perfluoro(N,N-dimethylethylamine) showed better fire-extinguishing ability than that of perfluorotriethylamine can not be explained for by physical supression mechanism only.

In order to get an insight into the behavior of CF_3 radical which can be formed as a result of the cleavage of the fragile C-N bond of $(CF_3)_3N$ during combusion, several model reactions of CF_3 radical in fire was studied by *ab initio* molecular orbital calculations.

It was revealed that CF_3-radical behaved catalitically as a radical scavenger for hydrogen and hydroxyl radicals, which exist abundantly during combustiuon, just like the role by a bromine radical generated from Halons (Figure 2). This special chemical action of CF_3-redical is considered as the secret of the better effectiveness for the former in fire supression due to the additional contribution of chemical supression by CF_3-radical between $(CF_3)_2NC_2F_5$ and $(C_2F_5)_3N$. Furthermore, an important methodology for the development of high efficiency Br-free Halon replacements was suggested: compounds which can emit as much as CF_3-redicals effectively on contact with fire will be good candidate for Halon replacements. Thus, polyfluoroamines, especially those having a $(CF_3)_2N$- group, showed great promise as new Halon replacements having good fire extingushing ability.

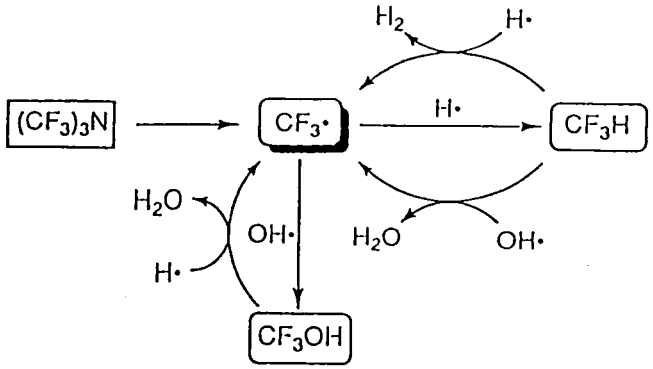

Figure 2. CF3-radical-mediated fire suppression mechanism

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