A-2.2.6 Studies on the Molecular Design of Highly Efficient Halon Replacements and Their Basic Evaluation as Fire Extinguishers

Contact Person Takashi Abe
Chief, Fluorine Chemistry Laboratory
National Industrial Research Institute of Nagoya
Agency of Industrial Science and Technology
1-1, Hirate-cho, Kita-ku, Nagoya 462-8510 Japan
Tel: 81-52-911-2111 (Ext. 2630), Fax: 81-52-916-2802
E-mail: abe@nirin.go.jp

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Key Words Halon alternatives, Fire extinguishers, Polyfluoroamines, polyfluoroethers, Polyfluorosulfur compound.

Abstract

The strategy for the development of bromine-free halon replacement with high fire-extinguishing ability is the use of as much as CF_3 radicals generated from fluorocompounds in fire, of which CF_3 radicals act the role of fire suppression played by the bromine atom. Thus, as the target bromine-free halon replacement, fluorine-containing compounds having the molecular structure in which CF_3- and C_2F_5- groups bonded directly to the hetero-atom (oxygen, nitrogen and sulfur) were synthesized and their fire extinguishing ability was evaluated by the measurement of laminar flame velocities of methane and heptane flames, and by the extinction test by a cup burner. It was found that among these compounds, polyfluoroamines showed the best fire extinguishing ability compared with polyfluorocompounds and those of O and S containing compounds. However, the latter two compounds showed comparable fire extinguishing ability to that of FM200 and FE23 which were put in practical use. For the explanation of good fire suppression of perfluoroamines represented by $(CF_3)_2NC_2F_5$, the computational chemistry study was conducted on the reaction of C_2F_5 radical with hydroxyl and hydrogen radical comparing with that of CF_3-radical. As far as the action between perfluoroalkyl radical and hydrogen and hydroxyl radicals in flame is concerned, it was found that C_2F_5-radical behaves more effectively than CF_3 radical as hydroxyl and hydrogen radical scavenger.

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

1. Introduction

The destruction of ozone layer has been the global environmental subject 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). Halons are gaseous fire fighting agents which have bromine atom, e.g. CF_3Br (Halon 1311), CF_2ClBr (Halon 1211), and CF_2BrCF_2Br (Halon 2402). As the high efficiency of halon fire extinguisher is due to the chemical fire suppression mechanism catalyzed by bromine atom[2], the lack of bromine atom in halon replacement results in a low extinguishing ability. However, bromine-containing compounds can not be used as halon replacements in view of the ozone depletion problem. This dilemma caused by the dual bromine action makes it difficult to develop ideal halon replacement .

2. Research objective

This project aims at the development of bromine-free halon replacement which has high fire-extinguishing ability. In order to impart the high fire-extinguishing ability to halon replacements, compounds which can easily generate CF_3 and C_2F_5 radicals in flame are selected as the promising candidate for it, as it has been found that CF_3 radical can mimic the fire suppression role played by the bromine atom [3]. Thus, as the target bromine-free halon replacement, fluorine containing compounds having the molecular structure in which CF_3- and C_2F_5- groups bonded directly to the heteroatom (oxygen, nitrogen and sulfur) were synthesized and their fire extinguishing ability was evaluated by the measurement of laminar flame velocities of methane and heptane flames, and the measurement of extinguishing concentration of additives by a cup-burner. Furthermore, for the explanation of fire-suppression mechanism by perfluoroalkyl radicals, the computational chemistry study was conducted in terms of the action of C_2F_5 radical comparing with that of CF_3-radical.

3. Research Method

Our new Halon replacements program consists of the preparation of the polyfluorocarbons containing N, O or S atoms, and the evaluation of fire-extinguishing ability for these compounds. In order to get insight into the secret of high fire extinguishing ability of bromine-free polyfluorocarbons especially represented by $(CF_3)_2NC_2F_5$, *ab initio* molecular orbital calculations were conducted for the actions of CF_3 and C_2F_5 radicals toward hydrogen radical and hydroxyl radical in the combustion zone.

(1) Preparation of new Halon substitutes

Perfluoroalkylamines and their derivatives, perfluoroethers, and perfluorosulfur compounds used in this experiments were made by means of electrochemical fluorination[4]. $(CF_3)_2NCF_2H$ and $(CF_3)_2NCF_2CF_2H$ were prepared by the decarbondioxide reaction of corresponding potassium salts of corresponding perfluoro(N,N-dimethylaminoacitic acid) and perfluoro(N,N-dimethylaminopropionic acid) in the presence of ethyleneglycol[5], respectively. $(CF_3)_2NCH_2CF_3$, $(CF_3)_2NCH_2CHF_2$, and $(CF_3)_2NC_2H_5$ were made by the reaction of perfluoro-2-azapropene with polyfluoroalkyl triflate ($CF_3S(O)_2OR_f$: R_f=polyfluoroalkyl group) in the presence of KF in an aprotic solvent. $CF_3OCHFCF_3$ and $CF_3OCF=CF_2$ were used as received.

(2) Evaluation of fire extinguishing ability

The evaluation of fire extinguishing ability for these compounds was done by measuring the burning velocities (laminar flame speed) of methane and heptane flames (A)[6] and also by an extinction test using a cup-burner (B)[7]. CF_3Br (Halon 1301), CO_2, CHF_3 (HFC-23, FE23; DuPont), CF_3CHFCF_3 (HFC227ea, FM200; Great Lakes), C_4F_{10} (CEA-410; 3M) were also investigated for a comparison. The first method (A) showed the inhibition effect on the burning velocities of the additives, of which order reflects that of the fire extinguishing ability. The second method (B) provided the data concerning the concentration of additives when the heptane flame is extinguished. In this case, for the calculation of the requisite heat capacities of several gases, MO calculations were conducted by MOPAC program using AM1 and PM3 Hamiltonians.

(3) Molecular orbital calculation

ab initio molecular orbital theory calculations were done with the Gaussian 94 program (G1, G2, and G2(MP2)) on the reactions of the pentafluoroethyl radical with the hydroxyl and the hydrogen radicals to estimate the fire suppression efficiency.

4. Result

Figure 1 shows the schematic diagram of combustion chamber for the measurement of laminar burning velocity, and Table 1 shows the summary of data of burning velocities of methane and heptane flames with aditives of polyfluorocarbons containing N, O and S atom. From these experiments, it was found that polyfluoroalkylamines showed excellent suppression effect on the burning compared with those of polyfluoroethers, and fluorine-containing sulfur compounds. Among polyfluoroalkylamines, $(CF_3)_3N$ and $(CF_3)_2NC_2F_5$ (decreasing ratio: 29.2% and 29.0%, respectively) showed comparable fire extinguishing ability to that (41.3%) of Halon 1301. Polyfluoroethers and polyfluorocarbons containing S showed comparable or better suppression effect to that of FM200. The exhausted gases from the combustion of sulfur compounds (CF_3SF_5, $C_2F_5SF_5$, and CF_3SO_2F) were irritant and stench in comparison with those from perfluoroethers and polyfluoroamines.

The ability as fire fighting agents is usually evaluated by an extinguishing test by a cup burner (B). Small scaled cup burner apparatus was used for the determination of several

Figure 1. Schematic diagram of combustion chamber[6)]

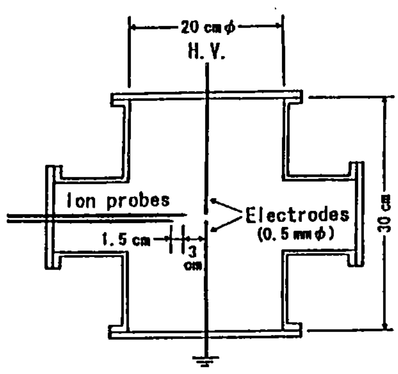

Table 2. Burning velocities (laminar flame speed) of methane and heptane flame with additives

Additives	Methane flame a)		Heptane flame b)	
	Observed / $cm.s^{-1}$	Decreasing ratio / %	Observed / $cm.s^{-1}$	Decreasing ratio / %
none	39.0	------	44.5	------
CO_2	38	3	41	3
CF_3Br (Halon1301)	22.9	41.3	31.1	30.1
CF_3CHFCF_3 (FM200)	33.7	13.6	38.0	14.6
CHF_3 (FE23)	35.0	10.3	38.6	13.3
C_4F_{10} (CEA410)	34.3	12.1	38.0	14.6
$(CF_3)_3N$	27.6	29.2	33.0	25.8
$(CF_3)_2NC_2F_5$	27.7	29.0	32.6	26.7
$(C_2F_5)_3N$	28.2	27.7	29.3	34.2
$(CF_3)_2NCF_2H$	28.3	27.4	33.4	24.9
$(CF_3)_2NCH_2CF_3$	28.8	27.4		
$(CF_3)_2NCF{=}CF_2$	28.8	26.2	34.0	23.6
$(CF_3)_2NCF_2CHF_2$	29.4	24.6	33.2	25.4
$(CF_3)_2NCH_2CHF_2$	30.8	21.0		
$(CF_3)_2NCH_2CH_3$	30.9	20.8		
CF_3OCF_3	33.8	13.3		
$C_2F_5OC_2F_5$	30.4	22.1	36.0	19.1
$C_2F_5SF_5$	30.7	21.3	35.7	19.8
CF_3SF_5	33.7	13.6	35.9	19.3
CF_3SO_2F	32.3	17.2		

a) mixtures of 9.50 vol% methane, 90.00 vol% air, and 0.50 vol% inhibitor.

b) mixtures of 1.87 vol% heptane, 97.63 vol% air, and 0.50 vol% inhibitor.

Figure 2. Cup burner apparatus

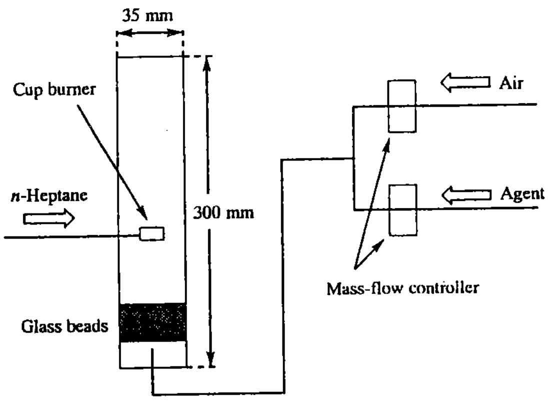

Table 2. Extinguishing Concentration

Agents	Lit. [a](%)	Extinguishing Concentration AM1[b]	Standard deviation	PM3[c]	Standard deviation
N_2		35.44	0.10		
CO_2	~22	19.32	0.08	19.25	0.08
CF_3Br	2.9~3.9	3.27	0.04	3.36	0.04
CF_3CHFCF_3 (FM200)	5.8~6.6	6.90	0.05	6.96	0.05
CHF_3	12.0~13.0	13.02	0.05	12.87	0.05
C_4F_{10}	5.0~5.9	6.02	0.03	6.13	0.03
$(CF_3)_3N$		5.31	0.09	5.32	0.09
$(CF_3)_2NC_2F_5$		5.18	0.08	5.21	0.08
$(CF_3)_2NCF_2H$		5.50	0.06	5.44	0.06
$CF_3OC_2F_5$		7.53	0.13	7.53	0.13
$CF_3OCHFCF_3$		11.05	0.12	10.95	0.11
$CF_3OCF=CF_2$		15.85	0.01	15.77	0.08

a) Montreal Protocol on Substrates that Deplete the Ozone Layer.
Report of the Halon Fire Extingushing Agents Technical Options Comitee, UNEP (1994, 12).

b) Using conversion factor calculated by AM1.

c) Using conversion factor calculated by PM3.

polyfluorocarbons containing N and O atom (Figure 2). Table 2 shows the data of extinguishing concentration by this method. Among the compounds tested, it was found that $(CF_3)_2NC_2F_5$ and $(CF_3)_3N$ showed the value (5.18~5.21% and 5.31~5.32%, respectively), which are next high value to that (3.27~3.36%) of Halon 1301. These compounds are one of the best fire suppressants among halon replacements which have already bee n reported.

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 $(CF_3)_3N$ and $(CF_3)_2NC_2F_5$ showed good fire-extinguishing ability compared with, for example, C_4F_{10} can not be explained for by physical suppression mechanism only. In order to get an insight into the behavior of CF_3 and C_2F_5 radicals which can be formed as a result of the cleavage of the fragile C-N bond of $(CF_3)_2NC_2F_5$ during combustion, several model reactions for these radicals in fire was studied by *ab initio* molecular orbital calculations.

It was revealed that both CF_3 and C_2F_5 radicals behaved catalytically as a radical scavenger for hydrogen and hydroxyl radicals, which exist abundantly during combustion, just like the role by a bromine radical generated from Halons. This special chemical action of CF_3 and C_2F_5 radicals is considered as the secret of the excellent fire suppression in conjunction with the easy emission of these radicals from perfluoroamines in fire. As far as the action between perfluoroalkyl radical and hydrogen and hydroxyl radicals in flame is concerned, it was found that C_2F_5-radical behaves more effectively than CF_3 radical as a hydrogen and hydroxyl radical scavenger: i.e. the former was easier to regenerate and more difficult to decompose than the latter. In view of the boiling points of polyfluoroamines [$(CF_3)_3N$: bp -10 °C, $(CF_3)_2NC_2F_5$: 21 °C] which were found to have excellent fire extinguishing ability, these compounds are considered to be prospective halon replacement for the use of streaming agent similar to the case of n-C_4F_{10} (bp 1 °C).

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