BURNING VELOCITIES OF HEPTANE FLAMES CONTAINING POLYFLUOROALKYLAMINES

Y. Sekiuji, K. Takahaski, and T. Inomata
Department of Chemistry
Sophia University
Kioi-cho 1, chiyoda-ku
Tokyo, JAPAN

T. Abe, H. Fukaya, and E. Hayashi
National Industrial Research Institute of **Nagoya**
Hirate-cho 1, Kita-ku
Nagoya, Aichi, JAPAN

G. Inoue
National Institute for **Environmental Studies**
Onogawa 16-2
Tsukuba, Ibaraki, JAPAN

Introduction

Halons such as CF_3Br, CF_2ClBr, and C_2F_4B have been used for many years as gaseous fire-extinguishers due to their high inhibition efficiencies. Because of the seriousness of ozone depletion in the stratosphere, severe restrictions were recently imposed on use of not only chlorofluorocarbons (CFCs) but also Halons. Although carbon dioxide is popularly used as one of Halon alternatives, its inhibition efficiency is much lower than those of Halons. Additionally, erroneous use of a CO_2 fire-extinguisher often causes death from suffocation.

Under these circumstances, the development of new Halon alternatives is proceeding rapidly on public and commercial bases. Numerous trials have shown that polyfluoroalkanes ($C_mH_nF_{2m-n+2}$) have fairly high inhibition efficiencies, although their inhibition mechanism is unknown. In the U. S. A., CF_3CHFCF_3 (FM200) has been marketed as a new fire-extinguisher substance sine 1993. The ozone depletion potentials (ODPs) of polyfluoroalkanes are nearly zero due to the absence of bromine and chlorine.

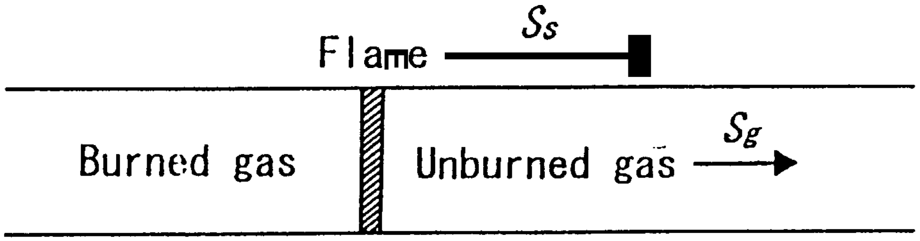
In this study, we focused on several polyfluoroalkylamines which could be used as Halon alternatives. To estimate the inhibition effect of polyfluoroalkylamines, laminar burning velocities were measured for n-heptane flames containing the inhibitors. The inhibition mechanism of polyfluoroalkylamines was suggested by a model calculation.

Experimental techniques to evaluate inhibition efficiencies of additives

Although many experimental techniques are used to evaluate inhibition efficiencies of additives, they are essentially divided into the following two measurements:

1. Inflammability limits
2. Burning velocity

Laminar burning velocity (S_u) is the relative velocity between the propagating velocity of flame (S_s) and the velocity of unburned gas ahead of flame (S_g), as shown in Fig. 0.



$$S_u = S_s - S_g \qquad (0)$$

Fig. 0 Schematic diagram for flame propagation.

Measurement of laminar burning velocity

Laminar burning velocities were determined using the density ratio method. The cylindrical combustion chamber used is shown in Fig. 1. A mixture of n-heptane, air, and inhibitor was introduced in the chamber and ignited by a electrical spark. The speed of the spherically propagating flame was measured by two ion probes.

As the flame propagates at constant pressure in the early stage, the flame speed (S_s) can be related to the burning velocity (S_u) by the expression

$$S_u = \frac{\rho_b}{\rho_u} S_s = \frac{M_b T_u}{M_u T_b} S_s \qquad (1)$$

where ρ, M, and T are mass density, mean molecular weight, and gas temperature, respectively. Subscript u and b mean the unburned and burned states, respectively. In Eq. (1), the adiabatic flame temperature was used as T_b. M_b was calculated from the concentrations of chemical species existing at equilibrium.

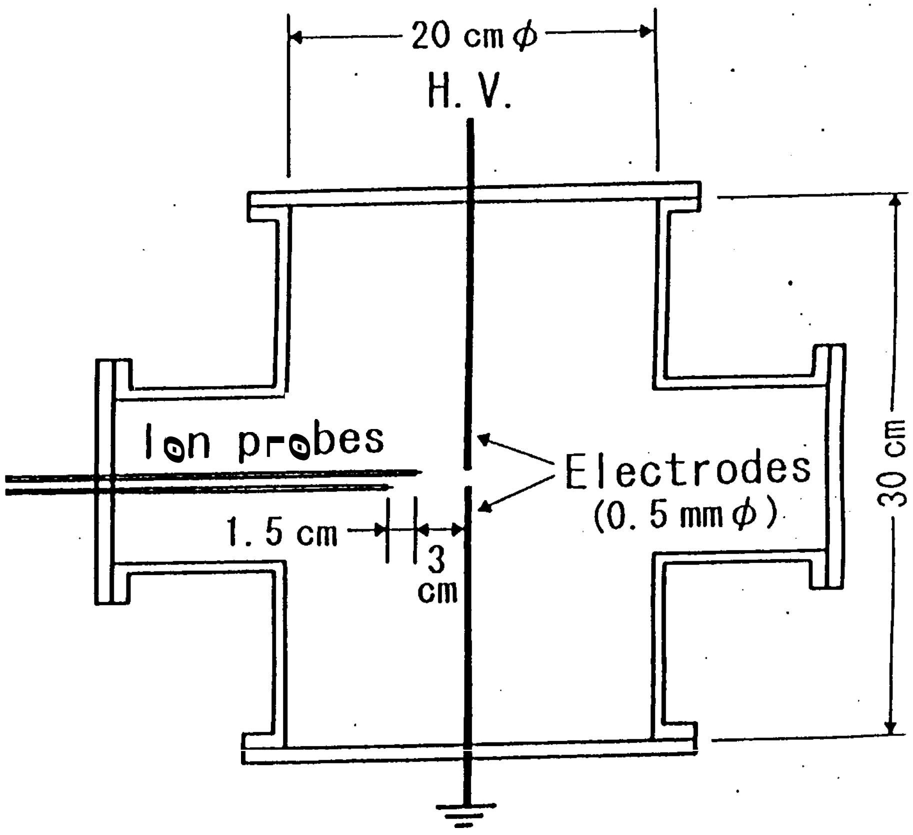


Fig. 1. Schematic diagram of combusti

Inhibitors tested in this study

All measurements were carried out with an initial temperature of 298±2 K and a pressure of 1 atm, using a mixture of 1.87 % n-heptane, 97.63 % air, and 0.50 % inhibitor.

The inhibitors are listed in Table I. As the focus of this work, three polyfluoroalkylamines were used. To be compared with the polyfluoroalkylamines, CF_3CHFCF_3 (FM200), CF_3Br (Halon 1301), and carbon dioxide which are used as fire-extinguishers were also examined. The polyfluoroalkylamines were synthesized by the authors, using the electrochemical fluorination method.

Table I Inhibitors tested in this study

Inhibitor	b. p. / ℃	Purity / %	Maker
$(CF_3)_2NCF_2CF_3$	20	$>$ 93	Prepared
$(CF_3)_2NCF_2CHF_2$	32	$>$ 97.5	Prepared
$(CF_3)_2NCF=CF_2$	14	$>$ 98.4	prepared
CF_3CHFCF_3 (FM200)	-15	$>$ 98	PCR Inc.
CF_3Br (Halon 1301)	-57	$>$ 99.5	Daikin Industries Ltd.
CH_3Br	4	$>$ 99	Tokyo Kasei Kogyo Co
CF_4	-128	$>$ 99.999	Daikin Industries Ltd.
CO_2	-79	$>$ 99.9	Nippon Sanso Co.

Model calculation of laminar burning velocity

To analyze the inhibition effect of additives on flame propagation, a computer simulation was performed. The equations governing steady, isobaric, one-dimensional flame propagation can be written as follows:

Conservation of energy;

$$\rho u c_p \frac{dT}{dx} - \frac{d}{dx}\left(\lambda \frac{dT}{dx}\right) + \sum_{i=1}^{I} \rho Y_i V_i c_{pi} \frac{dT}{dx} + \sum_{i=1}^{I} \omega_i h_i M_i = 0 \qquad (2)$$

Conservation of chemical species;

$$\rho u \frac{dY_i}{dx} + \frac{d(\rho Y_i V_i)}{dx} - \omega_i M_i = 0. \qquad (3)$$

c_p : mean specific heat at constant pressure
h_i : specific enthalpy of the i species
i : species index
T : gas temperature
V_i : diffusion velocity of the i species
Y_i : mass fraction of the i species
ρ : mass density
c_{pi} : specific heat at constant pressure of the i species
I : total number of chemical species
M_i : molecular weight of the i species
u : gas velocity
x : spatial coordinate
λ : mean thermal conductivity
ω_i : chemical production rate of the i species

The mass flux ($\rho u = \rho_u S_u$) is an eigenvalue in Eqs. (2) and (3). To obtain it, Eqs. (2) and (3) were numerically solved using the finite difference approximation under the following two boundary conditions:

$$T = T_u \text{ and } \frac{dT}{dx} = 0, \; Y_i = Y_{ui} \text{ and } \frac{dY_i}{dx} = 0 \quad \text{at } x = +\infty, \qquad (4)$$

$$T = T_b \text{ and } \frac{dT}{dx} = 0, \; Y_i = Y_{bi} \text{ and } \frac{dY_i}{dx} = 0 \quad \text{at } x = -\infty. \qquad (5)$$

Reaction mechanism for n-heptane oxidation

Table II. Reaction mechanism for n-heptane oxidation.
Rate coefficients in the form $k=AT^n \exp(-E/RT)$, in cm^3-mol-s-kJ-K units.

	Reaction	log A	n	E
R1	$H+O_2 \rightarrow OH+O$	17.08	-0.91	69.1
R2	$OH+O \rightarrow H+O_2$	15.85	-0.91	0.0
R3	$O+H_2 \rightarrow OH+H$	7.18	2.00	31.6
R4	$OH+H \rightarrow O+H_2$	6.83	2.00	23.3
R5	$OH+H_2 \rightarrow H_2O+H$	8.00	1.60	13.8
R6	$H_2O+H \rightarrow OH+H_2$	8.66	1.60	77.7
R7	$OH+OH \rightarrow H_2O+O$	9.18	1.14	0.0
R8	$H_2O+O \rightarrow OH+OH$	10.18	1.14	72.2
R9	$H+H+M \rightarrow H_2+M$	18.26	-1.00	0.0
R10	$H+OH+M \rightarrow H_2O+M$	22.34	-2.00	0.0
R11	$H+O_2+M \rightarrow HO_2+M$	18.30	-0.80	0.0
R12	$H+HO_2 \rightarrow OH+OH$	14.18	0.00	4.2
R13	$H+HO_2 \rightarrow H_2+O_2$	13.40	0.00	2.9
R14	$O+HO_2 \rightarrow OH+O_2$	13.30	0.00	0.0
R15	$OH+HO_2 \rightarrow H_2O+O_2$	13.30	0.00	0.0
R16	$CO+OH \rightarrow CO_2+H$	6.64	1.50	-3.1
R17	$CO_2+H \rightarrow CO+OH$	14.20	0.00	110.0
R18	$CH_3+H \rightarrow CH_4$	16.78	-1.00	0.0
R19	$CH_4+H \rightarrow CH_3+H_2$	4.34	3.00	36.6
R20	$CH_3+H_2 \rightarrow CH_4+H$	2.82	3.00	32.4
R21	$CH_4+O \rightarrow CH_3+OH$	7.08	2.10	31.9
R22	$CH_3+OH \rightarrow CH_4+O$	5.11	2.10	19.6
R23	$CH_4+OH \rightarrow CH_3+H_2O$	6.20	2.10	10.3
R24	$CH_3+H_2O \rightarrow CH_4+OH$	5.46	2.10	70.3
R25	$CH_3+O \rightarrow CH_2O+H$	13.85	0.00	0.0
R26	$CH_2O+H \rightarrow HCO+H_2$	13.40	0.00	16.7
R27	$CH_2O+O \rightarrow HCO+OH$	13.54	0.00	14.7
R28	$CH_2O+OH \rightarrow HCO+H_2O$	13.48	0.00	5.0
R29	$HCO+H \rightarrow CO+H_2$	14.30	0.00	0.0
R30	$HCO+O \rightarrow CO+OH$	13.48	0.00	0.0
R31	$HCO+O \rightarrow CO_2+H$	13.48	0.00	0.0
R32	$HCO+OH \rightarrow CO+H_2O$	13.70	0.00	0.0
R33	$HCO+O_2 \rightarrow CO+HO_2$	12.48	0.00	0.0
R34	$HCO+M \rightarrow CO+H+M$	14.85	0.00	70.3
R35	$CH_2+H \rightarrow CH+H_2$	13.60	0.00	0.0
R36	$CH_2+O \rightarrow CO+H+H$	13.70	0.00	0.0
R37	$CH_2+O_2 \rightarrow CO_2+H+H$	13.11	0.00	6.3
R38	$CH_2+CH_3 \rightarrow C_2H_4+H$	13.60	0.00	0.0
R39	$CH+O \rightarrow CO+H$	13.60	0.00	0.0
R40	$CH+O_2 \rightarrow CO+OH$	13.30	0.00	0.0
R41	$CH_3+CH_3 \rightarrow C_2H_6$	14.38	-0.40	0.0
R42	$CH_3+CH_3 \rightarrow C_2H_5+H$	13.90	0.00	111.0
R43	$CH_3+CH_3 \rightarrow C_2H_4+H_2$	16.00	0.00	134.0
R44	$C_2H_6+H \rightarrow C_2H_5+H_2$	2.73	3.50	21.8
R45	$C_2H_6+O \rightarrow C_2H_5+OH$	7.48	2.00	21.4
R46	$C_2H_6+OH \rightarrow C_2H_5+H_2O$	6.80	2.00	2.7
R47	$C_2H_5+H \rightarrow CH_3+CH_3$	13.48	0.00	0.0
R48	$C_2H_5+O \rightarrow CH_3HCO+H$	13.70	0.00	0.0
R49	$C_2H_5+O_2 \rightarrow C_2H_4+HO_2$	13.30	0.00	20.9
R50	$C_2H_5 \rightarrow C_2H_4+H$	13.30	0.00	166.0

Reaction mechanism for n-heptane oxidation (continured)

Table II. Reaction mechanism for n-heptane oxidation *(continued)*.

	Reaction	log *A*	m	*E*		Reaction	log A	*n*	a
R51	$C_2H_4+H \rightarrow C_2H_5$	13.00	0.00	6.3	R77	$C_3H_8+H \rightarrow n\text{-}C_3H_7+H_2$	14.11	0.00	40.6
R52	$C_2H_4+O \rightarrow HCO+CH_3$	9.20	1.20	3.1	R78	$C_3H_8+H \rightarrow i\text{-}C_3H_7+H_2$	14.00	0.00	34.9
R53	$C_2H_4+OH \rightarrow C_2H_3+H_2O$	13.85	0.00	12.6	R79	$C_3H_8+O \rightarrow n\text{-}C_3H_7+OH$	13.48	0.00	24.1
R54	$C_2H_4+H \rightarrow C_2H_3+H_2$	14.18	0.00	42.7	R80	$C_3H_8+O \rightarrow i\text{-}C_3H_7+OH$	13.41	0.00	18.7
R55	$C_2H_3+H \rightarrow C_2H_2+H_2$	13.30	0.00	0.0	R81	$C_3H_8+OH \rightarrow n\text{-}C_3H_7+H_2O$	12.57	0.00	6.9
R56	$C_2H_3+O_2 \rightarrow C_2H_2+HO_2$	12.00	0.00	0.0	R82	$C_3H_8+OH \rightarrow i\text{-}C_3H_7+H_2O$	12.45	0.00	3.6
R57	$C_2H_3 \rightarrow C_2H_2+H$	15.00	0.00	178.0	R83	$n\text{-}C_3H_7+H \rightarrow C_3H_8$	13.30	0.00	0.0
R58	$C_2H_2+H \rightarrow C_2H_3$	12.74	0.00	10.1	R84	$i\text{-}C_3H_7+H \rightarrow C_3H_8$	13.30	0.00	0.0
R59	$C_2H_2+O \rightarrow CH_2+CO$	8.61	1.50	7.1	R85	$n\text{-}C_3H_7+O_2 \rightarrow C_3H_6+HO_2$	12.00	0.00	20.9
R60	$C_2H_2+OH \rightarrow CH_2CO+H$	12.48	0.00	4.6	R86	$i\text{-}C_3H_7+O_2 \rightarrow C_3H_6+HO_2$	12.00	0.00	12.5
R61	$CH_3HCO+H \rightarrow CH_3+CO+H$	13.60	0.00	17.6	R87	$n\text{-}C_3H_7 \rightarrow C_2H_4+CH_3$	14.48	0.00	138.0
R62	$CH_3HCO+O \rightarrow CH_3+CO+OH$	12.70	0.00	7.5	R88	$n\text{-}C_3H_7 \rightarrow C_3H_6+H$	14.00	0.00	156.1
R63	$CH_3HCO+OH \rightarrow CH_3+CO+H_2O$	13.00	0.00	0.0	R89	$i\text{-}C_3H_7 \rightarrow C_3H_6+H$	14.30	0.00	161.9
R64	$CH_2CO+H \rightarrow CH_3+CO$	12.85	0.00	12.6	R90	$C_3H_6+H \rightarrow n\text{-}C_3H_7$	12.60	0.00	11.0
R65	$CH_2CO+O \rightarrow HCO+HCO$	13.30	0.00	9.6	R91	$C_3H_6+H \rightarrow i\text{-}C_3H_7$	12.60	0.00	4.0
R66	$CH_2CO+OH \rightarrow CH_2+HCO$	13.00	0.00	0.0	R92	$C_3H_6+H \rightarrow C_3H_5+H_2$	12.70	0.00	6.3
R67	$CH_2CO+M \rightarrow CH_2+CO+M$	16.00	0.00	248.0	R93	$C_3H_6+O \rightarrow C_2H_5+HCO$	12.55	0.00	0.0
R68	$C_2H_2+O \rightarrow HCCO+H$	14.63	0.00	50.7	R94	$C3H5+O_2 \rightarrow C_3H_4+HO_2$	11.78	0.00	41.8
R69	$HCCO+H \rightarrow CH_2+CO$	13.48	0.00	0.0	R95	$C_3H_4+OH \rightarrow C_2H_4+HCO$	12.00	0.00	0.0
R70	$HCCO+O \rightarrow CO+CO+H$	12.08	0.00	0.0	R96	$C_3H_4+O \rightarrow C_2H_3+HCO$	12.00	0.00	0.0
R71	$C_2H_2+H \rightarrow C_2H+H_2$	14.18	0.00	79.6	R97	$C_3H_6+OH \rightarrow CH_3HCO+CH_3$	13.00	0.00	0.0
R72	$C_2H_2+OH \rightarrow C_2H+H_2O$	13.00	0.00	29.3	R98	$C_7H_{16}+H \rightarrow C_7H_{15}+H_2$	6.65	2.00	20.9
R73	$C_2H+O \rightarrow CO+CH$	13.00	0.00	0.0	R99	$C_7H_{16}+O \rightarrow C_7H_{15}+OH$	13.15	0.00	21.7
R74	$C_2H+H_2 \rightarrow C_2H_2+H$	12.54	0.00	8.8	R100	$C_7H_{16}+OH \rightarrow C_7H_{15}+H_2O$	8.81	0.12	2.9
R75	$C_2H+O_2 \rightarrow CO+HCO$	13.70	0.00	6.3	R101	$C_7H_{15} \rightarrow C_3H_6+C_3H_6+CH_3$	13.20	0.00	142.0
R76	$C_2H_5+CH_3 \rightarrow C_3H_8$	12.85	0.00	0.0	R102	$C_7H_{15} \rightarrow C_3H_6+C_2H_5+C_2H_4$	13.20	0.00	138.0

Reactions involving bromic and fluoric species

Table III. Reversible reactions involving bromic and fluoric species.
Forward rate coefficients in the form $k_f = AT^{n_f}\exp(-E_f/RT)$, in cm^3-mol-s-kJ-K units.
Reverse rate coefficients (k_r) were calculated from k_f and equilibrium constants.

Reaction	$\log A_f$	n_f	E_f	Reaction	$\log A_f$	n_f	E_f
R103 $CH_3Br \Leftrightarrow CH_3 + Br$	13.50	0.00	300.0	R128 $CF_3 + CH_4 \Leftrightarrow CF_3H + CH_3$	12.00	0.30	46.0
R104 $CH_3Br + H \Leftrightarrow CH_3 + HBr$	14.24	0.00	28.9	R129 $CF_3 + CH_3 \Leftrightarrow CH_2CF_2 + HF$	13.83	0.60	0.0
R105 $CH_3Br + Br \Leftrightarrow CH_3 + Br_2$	13.70	0.00	95.8	R130 $CF_3 + O_2 \Leftrightarrow CF_2O + FO$	11.84	0.60	37.9
R106 $CF_3Br \Leftrightarrow CF_3 + Br$	13.70	0.00	277.4	R131 $CF_3H + M \Leftrightarrow CF_3 + H + M$	15.45	0.00	461.5
R107 $CF_3Br + H \Leftrightarrow CF_3 + HBr$	14.34	0.00	39.6	R132 $CF_3H \Leftrightarrow CF_2 + HF$	12.08	0.60	263.6
R108 $CF_3Br + Br \Leftrightarrow CF_3 + Br_2$	13.78	0.00	96.2	R133 $CF_3H + H \Leftrightarrow CF_3 + H_2$	12.70	0.60	20.9
R109 $CF_3Br + CH_3 \Leftrightarrow CF_3 + CH_3Br$	12.99	0.00	21.8	R134 $CF_3H + O \Leftrightarrow CF_3 + OH$	13.30	0.60	38.5
R110 $CF_4 \Leftrightarrow CF_3 + F$	15.95	0.00	503.8	R135 $CF_3H + OH \Leftrightarrow CF_3 + H_2O$	12.51	0.60	15.8
R111 $CF_4 + H \Leftrightarrow CF_3 + HF$	15.04	0.00	186.6	R136 $CF_3H + Br \Leftrightarrow CF_3 + HBr$	13.30	0.60	96.2
R112 $CF_4 + F \Leftrightarrow CF_3 + F_2$	14.02	0.00	363.2	R137 $CH_2CF_2 + O \Leftrightarrow CF_2O + CH_2$	13.18	0.60	0.0
R113 $HBr + H \Leftrightarrow H_2 + Br$	11.88	0.50	4.6	R138 $CH_2CF_2 + O \Leftrightarrow CF_2 + CH_2O$	13.18	0.00	0.0
R114 $HBr + O \Leftrightarrow OH + Br$	14.00	0.00	0.0	R139 $CH_2CF_2 + OH \Leftrightarrow CF_2O + CH$	13.00	0.00	4.2
R115 $HBr + OH \Leftrightarrow H_2O + Br$	14.00	0.00	0.0	R140 $CF_2O + H \Leftrightarrow FCO + HF$	11.11	0.60	0.0
R116 $Br_2 + H \Leftrightarrow HBr + Br$	12.81	0.50	4.6	R141 $CF_2O + O \Leftrightarrow FCO + FO$	12.70	0.40	19.2
R117 $Br + Br + M \Leftrightarrow Br_2 + M$	16.30	0.00	0.0	R142 $CF_2O + OH \Leftrightarrow FCO + HOF$	11.98	0.00	0.0
R118 $Br + H + M \Leftrightarrow HBr + M$	18.30	-0.71	0.0	R143 $CF_2 + H \Leftrightarrow C\ FHF$	13.00	0.60	0.0
R119 $Br + CH_4 \Leftrightarrow CH_3 + HBr$	14.00	0.00	76.6	R144 $CF_2 + O \Leftrightarrow FCO + F$	13.00	0.00	0.0
R120 $HF + H \Leftrightarrow H_2 + F$	14.34	0.00	141.2	R145 $CF_2 + OH \Leftrightarrow FCO + HF$	13.00	0.00	0.0
R121 $F_2 + H \Leftrightarrow HF + F$	14.08	0.00	10.0	R146 $CF_2 + OH \Leftrightarrow CF_2O + H$	13.00	0.60	0.0
R122 $F + F + M \Leftrightarrow F_2 + M$	14.00	0.00	0.0	R147 $CF_2 + CH_3 \Leftrightarrow CH_2CF_2 + H$	13.30	0.60	0.0
R123 $F + H + M \Leftrightarrow HF + M$	17.98	-1.00	0.0	R148 $FCO + M \Leftrightarrow CO + F + M$	14.16	0.60	125.5
R124 $F + CH_4 \Leftrightarrow CH_3 + HF$	14.00	0.00	5.1	R149 $FCO + H \Leftrightarrow CO + HF$	14.30	0.60	0.0
R125 $CF_3 + H \Leftrightarrow CF_2 + HF$	12.60	0.00	0.0	R150 $FCO + O \Leftrightarrow CO + FO$	14.00	0.00	0.0
R126 $CF_3 + O \Leftrightarrow CF_2O + F$	14.11	0.00	8.4	R151 $FCO + OH \Leftrightarrow CO + HOF$	14.00	0.40	0.0
R127 $CF_3 + OH \rightarrow CF_2O + HF$	12.60	0.00	0.0	R152 $FCO + OH \rightarrow CO_2 + HF$	14.00	0.60	0.0

Measured burning velocities of heptane flames with C_1-compounds

The inhibition mechanism of fluorinated C_1-compounds gives us valuable information to guide research on higher polyfluorocarbons. Figure 2 shows the laminar burning velocities (S_u) of n-heptane flames containing the C_1-compounds. CF_3Br reduces S_u by about 29 %, while CH_3Br reduces S_u only by about 24 %. The role of bromine in the bromic inhibitors has been clarified by numerous workers. HBr, Br, and Br_2 formed from the inhibitors act by catalyzing the recombination of H atoms into relatively non-reactive H_2 molecules, decreasing the rate of the chain branching reaction $H+O_2 \rightarrow OH+O$:

$HBr+H \rightarrow H_2+Br$ (R113) $Br_2+H \rightarrow HBr+Br$ (R116)

$Br+Br+M \rightarrow Br_2+M$ (R117) $Br+H+M \rightarrow HBr+M$ (R118)

If the inhibition effect of CF_3Br is caused only by this chain cycle, the difference in the inhibition efficiencies between CF_3Br and CH_3Br cannot be interpreted. CF_3 radicals produced from CF_3Br seem to contribute to the higher inhibition efficiency of CF_3Br.

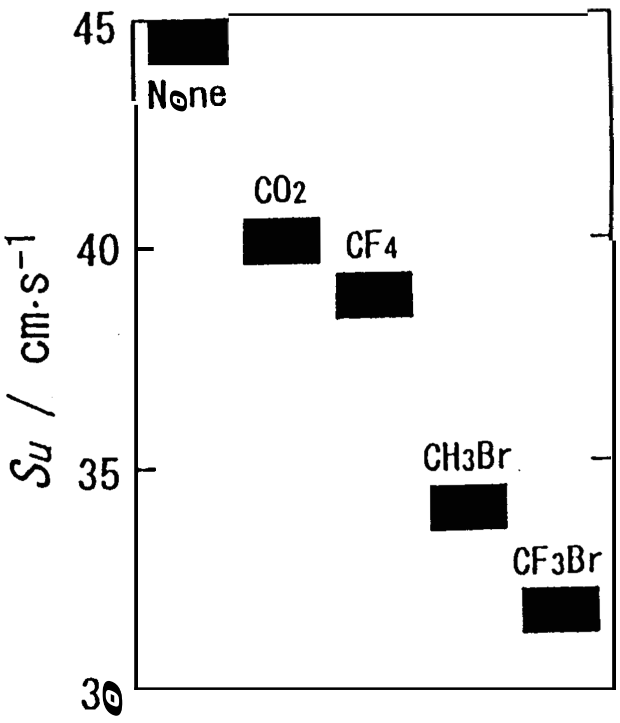


Fig. 2. Measured burning velocities of n-heptane flames with C_1-compounds.

Comparison of calculated and observed burning velocities of heptane flames with C_1-compounds

To clarify the role of CF_3 radicals in the flame, a computer simulation was carried out for n-heptane flames containing CH_3Br, CF_3Br, and CF_4, using the reaction model shown in Tables II and III. The calculated burning velocities are shown in Table IV, together with the observed ones. For all inhibited flames, the calculated burning velocities are larger than the observed ones. However, the calculation qualitatively expresses the experimental feature that CF_3Br has the highest inhibition efficiency and CF_4 has the lowest one in the three inhibitors.

Table IV. Comparison of calculated and observed burning velocities of heptane flames with C_1-compounds.

Inhibitor	S_u / cm·s^{-1}	
	calc.	obs.
None	45	45
CF_4	41	39
CH_3Br	36	34
CF_3Br	34	32

Decomposition process for CF_3 radicals

The simulation indicates that CF_3 radicals decompose through the pathway summarized in Fig. 3. In this pathway, fluoric species capture H, O, and OH radicals to become F atoms or stable HF molecules. The fluorine atoms are immediately consumed through the recombination and abstraction reactions, producing HF molecules.

As H, O, and OH radicals are chain carriers important for combustion reactions, the removal of these chain carriers by fluoric species causes the higher inhibition efficiency of CF_3Br. The chain cycle is not formed for these fluoric species because the produced HF molecules are very stable and the forward rate coefficient for reaction (R120) is much smaller than that for reaction (R113).

$$HF+H \rightarrow H_2+F \qquad (R120)$$

$$HBr+ \rightarrow H_2+Br \qquad (R113)$$

Therefore, the inhibition efficiency per fluorine atom is lower than the efficiency per bromine atom.

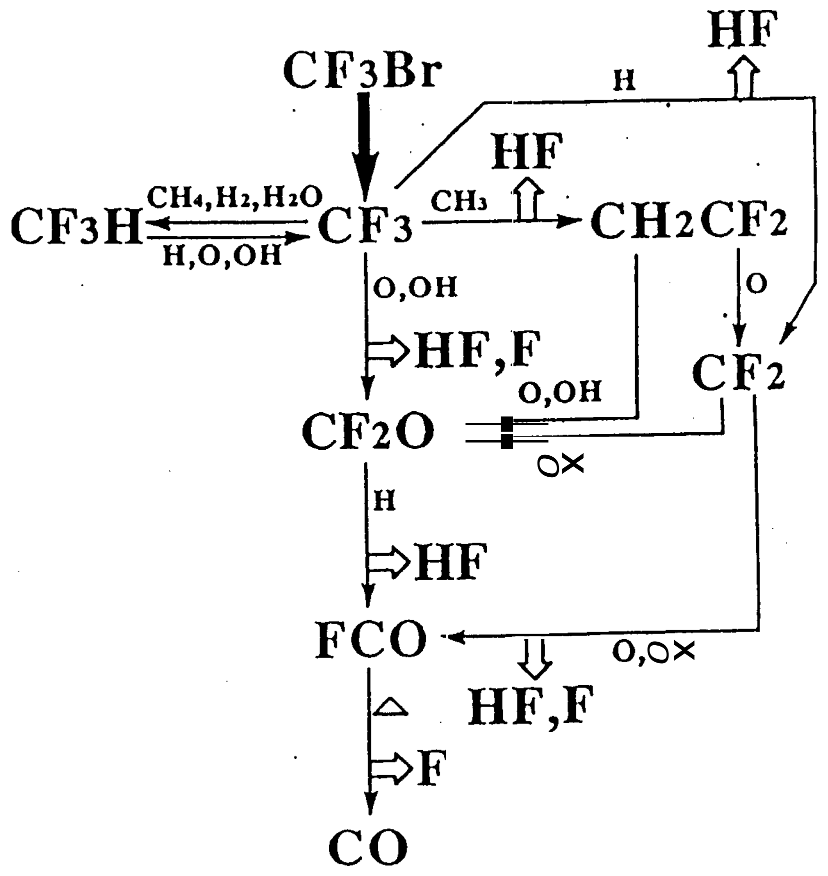


Fig. 3. Decomposition for CF_3 process.

Measured burning velocities of heptane flames with polyfluoroalkylamines

Figure 4 shows the laminar burning velocities of n-heptane flames containing the polyfluoroalkylamines. The polyfluoroalkylamines reduce S_u by 23-27 %. All of the polyfluoroalkylamines inhibit flame propagation less than CF_3Br (Halon 1301), but more than CF_3CHFCF_3 (FM200). This result shows that the polyfluoroalkylamines may be new fire-extinguishers having higher efficiencies than FM200.

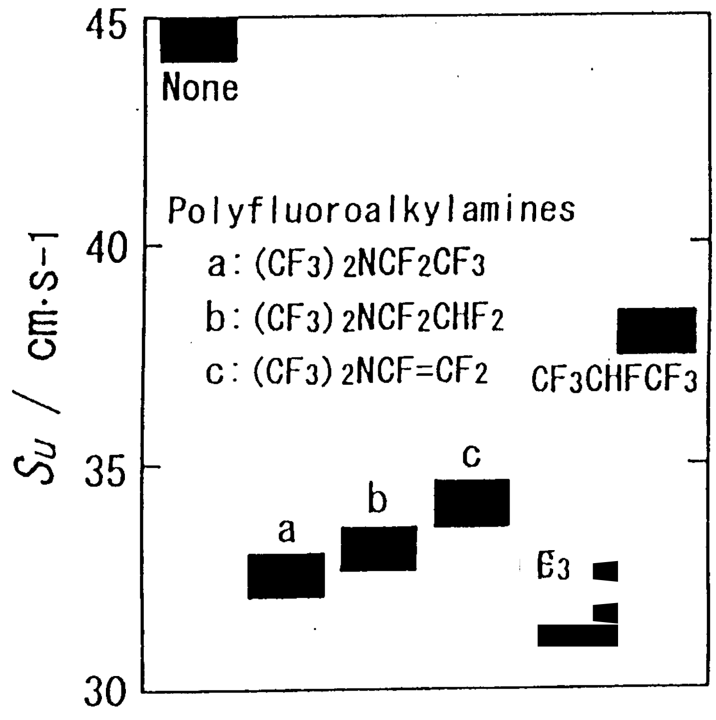


Fig. 4. Measured burning velocities of n-heptane flames with polyfluoroalkylamines.

General mechanism for combustion inhibition by additives

The inhibition effects of additives on flame propagation are generally divided into the following two types:

1. Dilution effect and physical effect caused by the change of transport and thermodynamic properties.

2. Chemical effect such as the removal of chain carriers important for combustion reactions.

Comparison of calculated and observed burning velocities of heptane flames with polyfluoroalkylamines

To estimate the degree of physical inhibition effect, a calculation was performed assuming that the polyfluoroalkylamines were inert (Table V). The calculation showed slow burning velocities for all mixtures. This means that the polyfluoroalkylamines have a large physical inhibition. However, the measured burning velocities are slower than the calculated ones. This fact suggests that the polyfluoroalkylamines have not only a physical inhibition effect, but also a chemical effect.

The chemical inhibition effect of polyfluoroalkylamines must be clarified by carrying out a simulation using a detailed reaction mechanism containing polyfluoroalkylamines. Although we cannot complete this calculation due to the absence of kinetic data, the above-mentioned discussion on CF_3 radicals makes us suggest that the chemical inhibition effect of polyfluoroalkylamines results from the removal of H, O, and OH radicals by fluoric species.

Table V. Comparison of calculated and observed burning velocities of heptane flames with polyfluoroalkylamines.

Inhibitor	S_u / cm·s^{-1}	
	calc. *	obs.
None	43	45
$(CF_3)_2NCF_2CF_3$	38	33
$(CF_3)_2NCF_2CHF_2$	38	33
$(CF_3)_2NCF=CF_2$	39	34

* Burning velocity calculated by assuming that each polyfluoroalkylamine is inert.

Difference of inhibition efficiencies between polyfluoroalkylamines and FM200

Figure 5 shows the reduction in burning velocities per fluorine atom ($-\Delta S_u/N_F$) against the number of fluorine atoms (N_F) in various polyfluoroalkylamines. The value of $-\Delta S_u/N_F$ increases with decreasing N_F. If an inhibition efficiency is dependent only on the number of fluorine atoms in fluorocarbons, CF_3CHFCF_3 (FM200) must be plotted on a line extrapolating the points of polyfluoroalkylamines. This tendency was not seen in the experiments.

Accordingly, the different inhibition efficiencies between polyfluoroalkylamines and FM200 seems to result from their thermal stabilities. The polyfluoroalkylamines decompose through the cleavage of C-N bond, while the polyfluoroalkanes such as FM200 do through the cleavage of C-C bond. As the C-N bond dissociation energy is lower than the C-C bond, polyfluoroalkylamines decompose more easily. Therefore, we suggest that the polyfluoroalkylamines have higher inhibition efficiencies than the polyfluoroalkanes, because they produce polyfluoroalkyl radicals in the lower temperature region of each flame.

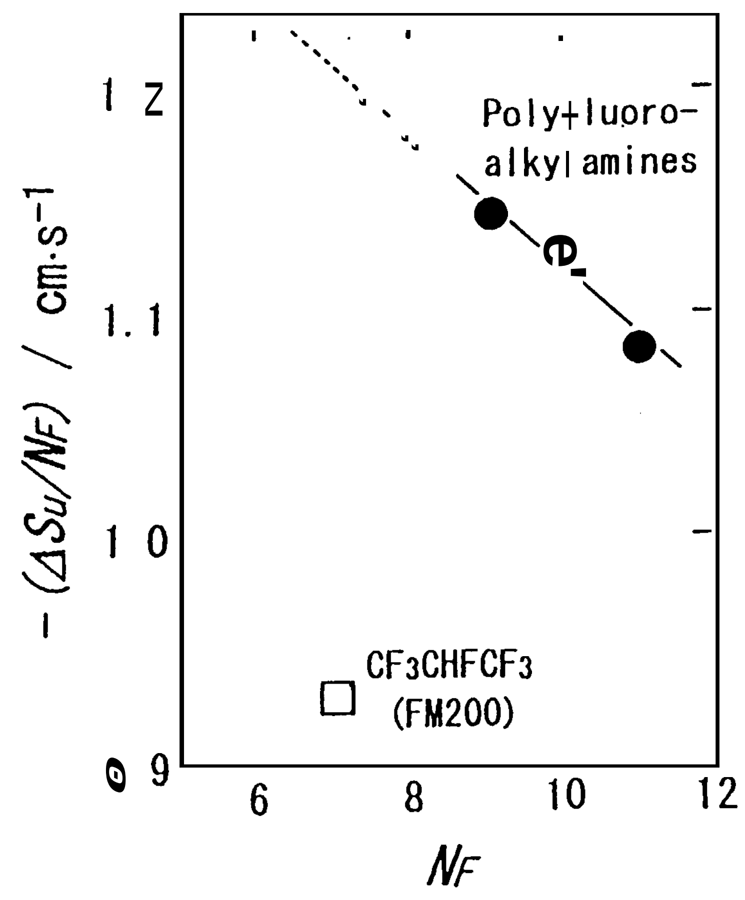


Fig. 5. Reduction in burning velocities per fluorine atom ($-\Delta S_u/N_F$) against the number of fluorine atoms (N_F).

Summary

To estimate the inhibition effect of several bromine- and chlorine-free polyfluoroalkylamines such as $(CF_3)_2NCF_2CF_3$, $(CF_3)_2NCF_2CHF_2$, and $(CF_3)_2NCF{=}CF_2$ on flame propagation, the laminar burning velocity was measured for a mixture of 1.87 % n-heptane, 97.63 % air, and 0.50 % inhibitor, at an initial temperature of 298±2 K and a pressure of atm.

All of the polyfluoroalkylamines inhibited flame propagation less than CF_3Br (Halon 1301), but more than CF_3CHFCF_3 (FM200). Calculation showed that the inhibition effect of polyfluoroalkylamines was caused not only by physical factors, but also by a chemical process in which fluoric species captured chain carriers (H, O, and OH) of combustion reactions to form stable HF molecules.

The inhibition efficiencies of polyfluoroalkylamines were found to be higher than those of polyfluoroalkanes such as FM200 because of polyfluoroalkylamines decomposition to reactive polyfluoroalkyl radicals in the lower temperature region of each flame.