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Ab Initio Molecular Orbital Study of Reaction of Pentafluoroethyl Radical with Hydroxyl and Hydrogen Radicals

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Ab initio molecular orbital theory calculations have been done on the reactions of the pentafluoroethyl radical with the hydroxyl and the hydrogen radicals to estimate its fire suppression efficiency. It was found that pentafluoroethyl radical was more effective than trifluoromethyl radical: i.e. the former was easier to regenerate and more difficult to decompose than the latter. The differences between the zero-point energies calculated by the HF and the MP2 method are also described.

Halons are perfluorinated carbons containing one or two bromine atoms such as CF_3Br (Halon 1301), CF_2BrCl (Halon 1211), and CF_2BrCF_2Br (Halon 2402). They were ideal fire suppression agents with high efficiency, low toxicity, cleanliness, and low electrical conductivity until the appearance of the ozone depletion problem. Conventional fire fighting agents, such as water and carbon dioxide, suppress the fire only by a physical action, i.e. cooling and dilution. Chemical suppression by removing the free radicals from the combustion zone is important in halon fire extinguishings.[1,2] Hydrogen atoms and hydroxyl radicals are considered to be the main active species in the combustion reaction. Bromine atoms from halons convert them to relatively unreactive H_2 or H_2O molecules by the following reactions:

$$Br\cdot + H\cdot \longrightarrow HBr$$

$$HBr + H\cdot \longrightarrow H_2 + Br\cdot$$

$$HBr + OH\cdot \longrightarrow H_2O + Br\cdot$$

The high efficiency of halon fire extinguishers is thought to be due to this suppression mechanism. Halons' use is, however, regulated because they are harmful to stratospheric ozone.

Bromine-containing compounds cannot be used as halon replacements in view of the ozone depletion problem, while non-bromine-containing compounds are not expected to have high fire suppression efficiency because of the lack of the chemical fire suppression played by bromine atoms. The dilemma caused by the dual bromine actions makes it difficult to develop a halon alternative. We found, however, that several perfluoroalkylamines having no bromine atom had a good fire extinguishing ability.[3,4] We proposed a new fire suppression mechanism for such non-bromine-containing perfluoroalkylamines in which the trifluoromethyl radical mimics the fire extinguishing role played by the bromine atom.[5,6]

The experimental data suggested that the perfluoroalkylamines with an trifluoromethyl group were more effective in chemical fire suppression than those having a pentafluoroethyl group.[4] The factors affected the extinguishing ability are (1) easiness of the generation of perfluoroalkyl radical from perfluoroalkylamines, (2) efficiency of perfluoroalkyl radical in chemical suppression, and (3) the other factors such as the reactions with O_2 or secondary products from fuel or extinguishers. In this paper, we describe whether it can explain the difference of extinguishing efficiencies between trifluoromethyl and pentafluoroethyl radicals on factor (2), i.e. the reactions of these radicals with the hydroxyl or the hydrogen radical.

Computational Methods

Ab initio molecular orbital calculations were done with the Gaussian 94 program.[7] The GAUSSIAN-1 (G1)[8] and GAUSSIAN-2 (G2)[9] theory calculations were used because they yielded energetics that were in far better agreement with experimental values.[6] All geometries were fully optimized at the MP2(FU)/6-31G* levels. Single point energy calculations were done at MP4/6-311G**, MP4/6-311+G**, MP4/6-311G**(2df), QCISD(T)/6-311G**, and MP2/6-311+G(3df,2p). The GAUSSIAN-2 theory using a second order Møller-Plesset level, G2(MP2),[10] was also used because G1 and G2 calculations on some species could not be done because of the limitation of our computational resources.

Results and Discussion

In our previous paper,[6] we described a theoretical study on the following reactions of the trifluoromethyl radical and its related species that are included in the fire suppression process:

$$CF_3\cdot + H\cdot \longrightarrow CF_3H \qquad (M1)$$

$$CF_3\cdot + OH\cdot \longrightarrow CF_3OH \qquad (M2)$$

$$CF_3H + H\cdot \longrightarrow CF_3\cdot + H_2 \qquad (M3)$$

$$CF_3H + OH\cdot \longrightarrow CF_3\cdot + H_2O \qquad (M4)$$

$$CF_3OH + H\cdot \longrightarrow CF_3\cdot + H_2O \qquad (M5)$$

$$CF_3\cdot \longrightarrow CH_2{:} + F\cdot \qquad (M6)$$

$$CF_3H \longrightarrow CF_2{:} + HF \qquad (M7)$$

$$CF_3OH \longrightarrow CF_2{=}O + HF \qquad (M8)$$

We report here the similar processes concerned with the pentafluoroethyl radical to discuss the difference of fire suppression ability of trifluoromethyl radical and pentafluoroethyl radical.

$$C_2F_5\cdot + H\cdot \longrightarrow C_2F_5H \qquad (E1)$$

$$C_2F_5\cdot + OH\cdot \longrightarrow C_2F_5OH \qquad (E2)$$

$$C_2F_5H + H\cdot \longrightarrow C_2F_5\cdot + H_2 \qquad (E3)$$

$$C_2F_5H + OH\cdot \longrightarrow C_2F_5\cdot + H_2O \qquad (E4)$$

$$C_2F_5OH + H\cdot \longrightarrow C_2F_5\cdot + H_2O \qquad (E5)$$

$$C_2F_5\cdot \longrightarrow CF_2{=}CF_2 + F\cdot \qquad (E6)$$

$$C_2F_5H \longrightarrow CF_2{=}CF_2 + HF \qquad (E7)$$

$$C_2F_5OH \longrightarrow CF_3COF + HF \qquad (E8)$$

Transition states were found in reactions (E3), (E4), (E5), (E7), and (E8); and the important parameters for them were depicted in Fig. 1. The transition states of pentafluoroethyl species TS3E, TS4E, and TS5E are found in the stage slightly earlier than those of trifluoromethyl ones, TS3M, TS4M, and TS5M; while the transition state TS7E is in later stage than TS7M: The lengths of C(1)–F(2) and H(3)–C(4) bonds in TS7E are 0.036 and 0.209 Å longer than those of C(1)–F(2) and H(3)–C(1) in TS7M, respectively; and that of F(2)–H(3) in TS7E is 0.047 Å shorter than the one in TS7M (Figs. 1 and 2). The transition states TS8E and TS8M have almost the same geometries about the reaction center, a four-membered ring of C(1)–O(4)–H(5)–F(3).

Though we used the harmonic frequencies calculated at the MP2(FU)/6-31G* level to estimate the zero-point energies (ZPEs) and thermal energy corrections (TEs) for the reactions of $CF_3\cdot$ in our previous paper,[6] those for the reactions of $C_2F_5\cdot$ were too expensive. We examined whether the HF method can be used for the calculations of ZPEs and TEs instead of the MP2 method. Table 1 shows the scaled ZPEs and TEs for the concerned species and states involved in the reactions (M1)—(M8). The differences between the HF and the MP2 methods do not exceed 1 milihartree[11] (0.6 kcal mol^{-1} [12]) for ZPE and 1.3 milihartree (0.8 kcal mol^{-1}) for TE. Table 2 shows the activation energies of reactions (M3), (M4), (M5), (M7), and (M8) using the ZPE calculated by the HF and the MP2 methods, respectively. The maximum differences were found in reaction (M5), but they were no more than 0.8 kcal mol^{-1}. Table 3 shows the heats of reactions of (M1)—(M8) at 298.15 K. The differences of heats of reactions between the HF and the MP2 were less than those of the activation energies, only 0.2 kcal mol^{-1}. Therefore, the HF method is quite enough and economical for the calculations of ZPEs or TEs.

Table 4 shows the G1, G2, and G2(MP2) Energies the species concerned with reactions (1)—(8). Table 5 shows the activation energies and heats of reactions of (E1)—(E8).

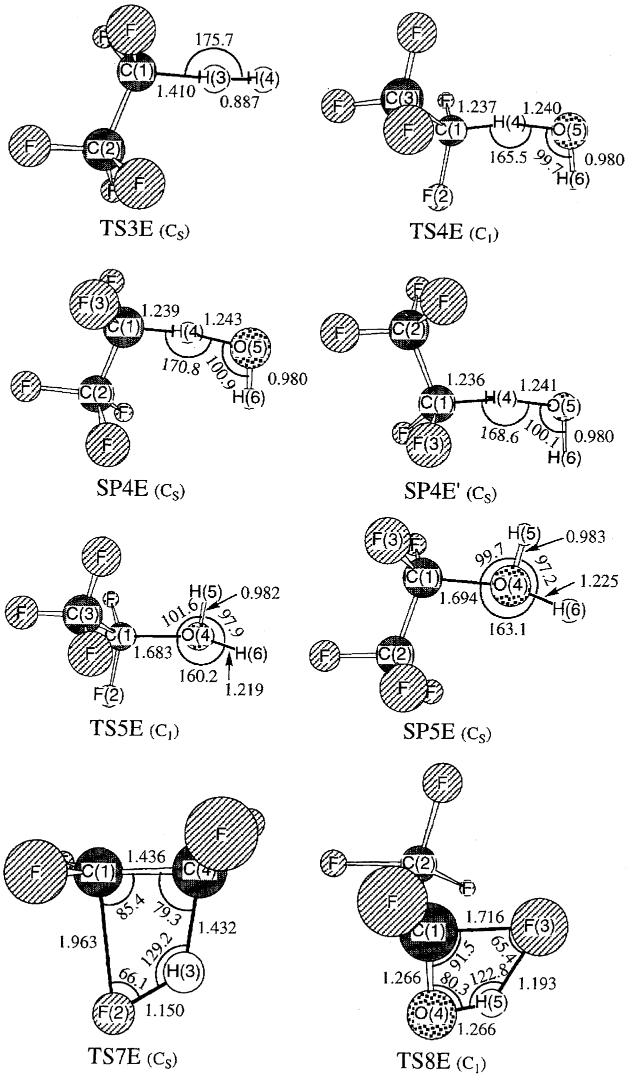

Fig. 1. Transition states and second-order saddle points concerned with pentafluoroethyl radical optimized at MP2(FU)/6-31G*. Bond lengths are given in ångstroms and angles in degrees.

Because the activation energies of the reactions of (E4) and (E5) could not be calculated by using the G1 and G2 theories because of the limitation of the computational resources, the G2(MP2) theory was also used. Since the results of the G2(MP2) were very close to those of the G2 theory (Tables 2, 3, and 5), we discussed the fire suppression abilities of $CF_3\cdot$ and $C_2F_5\cdot$ radicals using the G2(MP2) theory.

Reactions (1) and (2) are the scavenging processes of the $H\cdot$ and $OH\cdot$ radicals by perfluoroalkyl radicals. These reactions were barrierless and exothermic in both $CF_3\cdot$ and $C_2F_5\cdot$ radicals. Reactions (3), (4), and (5) are regeneration processes of the perfluoroalkyl radicals. The activation energies for the regeneration of $C_2F_5\cdot$ radical [12.9, 4.7, and 38.6 kcal mol^{-1} for reactions (3E), (4E), and (5E), respectively] were less than those of $CF_3\cdot$ radical [14.8, 6.5, and 41.4 kcal mol^{-1} for reactions (M3), (M4), and (M5), respectively]. These energetics are consistent with the geometries of early transition states of TS3E, TS4E, and TS5E when

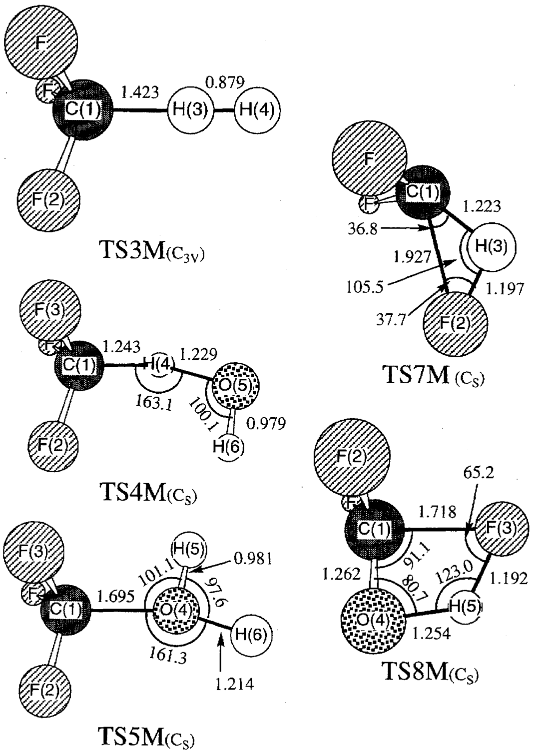

Fig. 2. Transition states concerned with trifluoromethyl radical optimized at MP2(FU)/6-31G*. Bond lengths are given in ångstroms and angles in degrees.

Table 1. Zero-Point Energies (ZPE) and Thermal Energies (TE)[a)]

Species & States	HF/6-31G* [b)]		MP2(FU)/6-31G* [c)]	
	ZPE	TE[d)]	ZPE	TE[d)]
$CF_3\cdot$	12.11	15.09	11.98	15.28
$H\cdot$	0.00	1.26	0.00	1.42
CF_3H	25.12	28.10	25.15	28.46
$OH\cdot$	8.12	10.23	8.19	10.46
CF_3OH	28.59	32.35	28.33	32.54
H_2	9.45	11.56	9.93	12.20
H_2O	20.51	23.04	20.64	23.37
$F_2C{=}O$	14.10	16.94	13.63	16.80
HF	8.86	10.97	8.85	11.12
CF_2:	6.93	9.58	6.85	9.72
$F\cdot$	0.00	1.26	0.00	1.42
TS3M	21.72	25.47	22.42	26.61
TS4M	29.34	34.59	29.88	35.56
TS5M	28.61	33.48	29.53	34.75
TS7M	18.21	21.76	18.01	21.82
TS8M	22.94	26.60	22.88	26.96

a) In milihartrees. b) Scaled by 0.8929. c) Ref. 6. d) At 298.15 K.

compared with TS3M, TS4M, and TS5M, respectively.

Table 2. Activation Energies (kcal mol^{-1})

Reaction	G1		G2		G2(MP2)	
	HF[a)]	MP2[b,c)]	HF[a)]	MP2[b,c)]	HF[a)]	MP2[b)]
M3	15.1	15.5	14.7	15.1	14.8	15.2
M4	6.6	6.9	6.4	6.7	6.5	6.8
M5	41.0	41.8	41.3	42.0	41.4	42.1
M7	73.3	73.1	73.3	73.2	73.3	73.1
M8	45.1	45.2	45.6	45.8	45.7	45.8

a) Using zero-point energy calculated by HF/6-31G*. b) Using zero-point energy calculated by MP2(FU)/6-31G*. c) Ref. 6.

Table 3. Heats of Reactions at 298.15 K (kcal mol^{-1})

Reaction	G1		G2		G2(MP2)	
	HF[a)]	MP2[b,c)]	HF[a)]	MP2[b,c)]	HF[a)]	MP2[b)]
M1	−107.4	−107.4	−108.0	−108.0	−108.0	−108.0
M2	−116.7	−116.9	−116.9	−117.1	−117.2	−117.4
M3	3.0	3.2	2.7	2.9	2.8	3.0
M4	−10.5	−10.6	−11.2	−11.3	−11.7	−11.8
M5	−1.2	−1.1	−2.2	−2.1	−2.6	−2.4
M6	83.2	83.2	84.0	84.1	84.0	84.1
M7	55.2	55.2	54.9	54.8	54.3	54.3
M8	7.2	7.1	7.8	7.7	7.6	7.5

a) Using thermal energy calculated by HF/6-31G*. b) Using thermal energy calculated by MP2(FU)/6-31G*. c) Ref. 6.

Reactions (6), (7), and (8) represent the decomposition of the perfluoroalkyl radicals and their related species. Reactions (6M) and (6E) had no transition state and were endothermic with large ΔH_s (84.0 and 74.1 kcal mol^{-1}, respectively). These reactions are negligible in comparison with reactions (1) and (2) if the relatively high concentration of H· or OH· is taken into account. Reactions (M8) and (E8) are the decomposition process of the products formed in reactions (M2) and (E2), respectively. The activation energies of reactions (M8) and (E8) were almost the same, reflecting the same geometries on the reaction center.

Reactions (M7) and (E7) are the decomposition process of the products formed in reactions (M1) and (E1), respectively. Though 1,2-dehydrofluorination was considered to occur easily, the activation energy of reaction (E7), 88.2 kcal mol^{-1}, was unexpectedly higher than that of (M7), 73.3 kcal mol^{-1}. The geometries between TS7E and TS7M, the former was later than the latter, were also considerably different. Since the 1,2-dehydrofluorination reaction of hydrofluorocarbon (HFC) is important from the viewpoint of the degradability of the replacements of halons as well as chlrofluorocarbons (CFCs), we will discuss on these reactions in another paper.

The reactions (E4) and (E5) had second order saddle points as depicted in Fig. 1. Replacing a fluorine atom in the C_s symmetry plane, F(2), of TS4M with the CF_3 group makes the second-order saddle points SP4E and SP4E′; while replacing a fluorine atom out of C_s plane, F(3), makes the transition states, TS4E. The lengths of C(1)–H(4) and H(4)–O(5) bonds were almost constant among TS4E, SP4E, and SP4E′, and the differences of energy among them were very small (Table 6). Although the symmetrical analogy was also seen in TS5E or SP5E, the geometries and energies were a little different: The length of the C(1)–O(4) bond in TS5E was shorter than that in SP5E by 0.011 Å, and SP5E was 1.0 kcal mol^{-1} above TS5E.

The trifluoromethyl group is known to have a negative

Table 4. The G1, G2, and G2(MP2) Energies at 0 K (E_0) and at 298.15 K (E_{298})[a)]

Species	G1 Energy		G2 Energy		G2(MP2) Energy	
& States	E_0	E_{298}	E_0	E_{298}	E_0	E_{298}
$CF_3\cdot$	−337.22135	−337.21838	−337.22371	−337.22073	−337.21341	−337.21044
$H\cdot$	−0.50000	−0.49874	−0.50000	−0.49874	−0.50000	−0.49874
CF_3H	−337.89035	−337.88737	−337.89357	−337.89059	−337.88336	−337.88037
$OH\cdot$	−75.64215	−75.64004	−75.64391	−75.64181	−75.64093	−75.63882
CF_3OH	−413.04726	−413.04350	−413.05170	−413.04794	−413.03887	−413.03511
H_2	−1.16501	−1.16290	−1.16636	−1.16425	−1.16636	−1.16425
H_2O	−76.32834	−76.32581	−76.33206	−76.32952	−76.33001	−76.32748
$F_2C{=}O$	−312.69081	−312.68796	−312.69134	−312.68850	−312.68189	−312.67905
HF	−100.34713	−100.34502	−100.35001	−100.34790	−100.34704	−100.34493
CF_2:	−237.45796	−237.45531	−237.45885	−237.45620	−237.45247	−237.44981
$F\cdot$	−99.63275	−99.63148	−99.63281	−99.63155	−99.62894	−99.62768
$C_2F_5\cdot$	−574.76852	−574.76328	−574.77163	−574.76640	−574.75432	−574.74908
C_2F_5H	−575.43290	−575.42771	−575.43675	−575.43156	−575.41953	−575.41434
C_2F_5OH	−650.59111	−650.58504	−650.59561	−650.58955	−650.57575	−650.56969
CF_3COF	−550.23211	−550.22700	−550.23393	−550.22882	−550.21752	−550.21241
C_2F_4	−475.02219	−475.01777	−475.02204	−475.01762	−475.00864	−475.00422
TS3M	−338.36624	−338.36250	−338.37016	−338.36641	−338.35973	−338.35598
TS4M	−413.52201	−413.51676	−413.52726	−413.52201	−413.51395	−413.50870
TS5M	−413.48188	−413.47701	−413.48591	−413.48105	−413.47291	−413.46805
TS7M	−337.77355	−337.77000	−337.77673	−337.77318	−337.76659	−337.76304
TS8M	−412.97542	−412.97175	−412.97900	−412.97533	−412.96610	−412.96243
TS3E	−575.91181	−575.90585	−575.91637	−575.91041	−575.89895	−575.89298
TS4E	—[b)]	—[b)]	—[b)]	—[b)]	−651.05293	−651.04538
TS5E	—[b)]	—[b)]	—[b)]	—[b)]	−651.01422	−651.00711
TS7E	−575.29276	−575.28701	−575.29627	−575.29051	−575.27900	−575.27324
TS8E	−650.51791	−650.51192	−650.52181	−650.51582	−650.50190	−650.49591
SP4E	—[b)]	—[b)]	—[b)]	—[b)]	−651.05290	−651.04602
SP4E′	—[b)]	—[b)]	—[b)]	—[b)]	−651.05284	−651.04597
SP5E	—[b)]	—[b)]	—[b)]	—[b)]	−651.01256	−651.00596

a) Zero-point energy and thermal energy corrections are calculated by HF/6-31G* level and scaled by 0.8929. In hartrees.
b) Could not be calculated.

Table 5. Activation Energies (E_a) and Heats of Reactions (ΔH) at 298.15 K (kcal mol^{-1})

Reaction	E_a			ΔH		
	G1	G2	G2(MP2)	G1	G2	G2(MP2)
E1	—[a)]	—[a)]	—[a)]	−104.6	−105.0	−105.1
E2	—[a)]	—[a)]	—[a)]	−114.6	−114.4	−114.7
E3	13.2	12.8	12.9	0.2	−0.2	−0.2
E4	—[b)]	—[b)]	4.7	−13.4	−14.2	−14.7
E5	—[b)]	—[b)]	38.6	−3.3	−4.8	−5.1
E6	—[a)]	—[a)]	—[a)]	72.1	74.2	74.1
E7	87.9	88.2	88.2	41.3	42.0	41.5
E8	45.9	46.3	46.3	8.8	8.6	8.3

a) No transition state was found. b) Could not be calculated.

Table 6. Energies of the Transition States and Second-Order Saddle Points of Reactions (E4) and (E5)

States	E(G2MP2)	Relative energy
	hartree	kcal mol^{-1}
TS4E	−651.05293	—
SP4E	−651.05290	0.016[a)]
SP4E′	−651.05284	0.057[a)]
TS5E	−651.01422	—
SP5E	−651.01256	1.045[b)]

a) Relative to TS4E. b) Relative to TS5E.

hyperconjugation effect.[13)] Because the CF_3 group acts as a strong π-acceptor due to the large electron-withdrawing ability of fluorine, it stabilizes an adjacent π-donating substitutent. The stabilizing effect of the CF_3 group is considered to affect at least the γ-position.[14)] The C(1)–H(4) bond lengths were almost constant among TS4M, TS4E, SP4E, and SP4E′, since the negative hyperconjugation effect on a hydrogen was relatively small due to a lack of a p-orbital on a hydrogen. Though the C(1)–O(4) bond in SP5E was the same as the one in TS5M, that in TS5E was shorter by 0.012 Å. This means that the rotational orientation of trifluoromethyl group on C(1)–O(4) bond affects the degree of the stabilization of C(1)–O(4) bond. The interaction between σ^* of C(1)–C(3) bond and a lone pair of O(4) could be a origin of the stabilization of the C(1)–O(4) bond in TS5E (Fig. 3).

Conclusions

The differences between the zero-point energies calculated by the HF and the MP2 method were less than 0.6 kcal mol^{-1}, and those of thermal energy corrections at 298 K were less than 0.8 kcal mol^{-1}. These differences affected the activa-

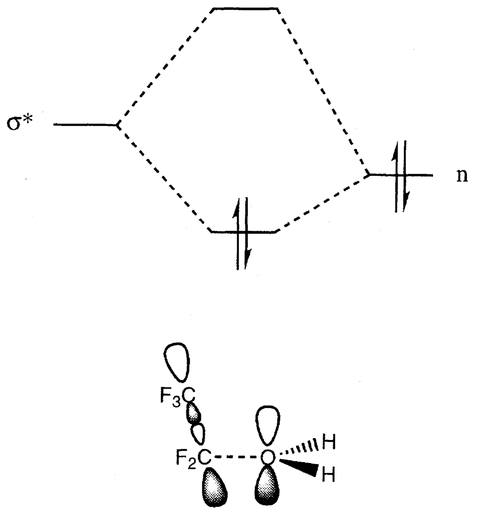

Fig. 3. Orbital interactions between σ^* and n in TS5E.

tion energies by no more than 0.8 kcal mol^{-1}, and the heats of reactions by 0.2 kcal mol^{-1}.

The G2(MP2) theory gave similar results on the activation energies and the heats of reactions to the G2 theory within 0.5 kcal mol^{-1}.

From the results of the G2(MP2) theory calculations, it was found that $C_2F_5\cdot$ radical was more effective in fire suppression than $CF_3\cdot$ radical: i.e. the former was easier to regenerate and more resistant to decomposition than the latter. So, we need also examine the factors (1) and (3) to discuss the difference of the fire extinguishing abilities between perfluoroalkylamines having CF_3 and C_2F_5 groups. Further research on the fire suppression mechanism of perfluoroalkyl radicals and the development of new halon replacement are underway in our laboratory.

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11) 1 hartree = 2.625×10^6 J mol^{-1}.

12) 1 cal = 4.184 J.

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