New Fire Suppression Mechanism of Perfluoroalkylamines

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Ab initio molecular orbital calculations on the reactions of the trifluoromethyl radical, which can be easily released from perfluoroalkylamine by dissociation of C–N bonds, with hydroxyl or hydrogen radicals revealed the fire extinguishing mechanism of non-bromine-containing halon replacements such as perfluoroalkylamines.

Halons, perfluorinated carbons containing bromine [*e.g.* CF_3Br (Halon 1301), CF_2BrCl (Halon 1211), CF_2BrCF_2Br (Halon 2402)], are gaseous fire extinguishing agents. Conventional fire fighting agents, such as water and carbon dioxide, suppress fire by cooling and dilution. Chemical suppression by removing the free radicals from the combustion zone is also important in halon fire extinguishing.[1,2] Hydrogen atoms and hydroxyl radicals are the main active species in combustion and are converted by bromine atoms from halons to relatively unreactive H_2 or H_2O molecules by the following catalytic cycle.

$$Br^{\cdot} + H^{\cdot} \rightarrow HBr$$

$$HBr + H^{\cdot} \rightarrow H_2 + Br^{\cdot}$$

$$HBr + OH^{\cdot} \rightarrow H_2O + Br^{\cdot}$$

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

We recently found that several specific perfluoroalkylamines showed good fire extinguishing properties comparable to those of halon 1301[3,4] and since bromine has a vital role, there should be a new, hitherto unknown mechanism involved.

To obtain an insight into the mechanism of the non-bromine-containing halon replacements, we conducted *ab initio* molecular orbital calculations using the GAUSSIAN 92 program.[5] First of all we considered a C–N bond dissociation which triggers the decomposition of perfluorotrimethylamine. Fig. 1 shows the C–N bond dissociation energy of perfluorotrimethylamine and its cation radical. Though the C–N bond dissociation energy of the neutral molecule is more than 470 kJ mol^{-1}, that of the cation radical is about 1/6 of the neutral one. Furthermore, the optimized geometry of the anion radical of perfluorotrimethylamine has a partly dissociated C–N bond (Fig. 2). So, perfluorotrimethylamine could easily release trifluoromethyl radicals by oxidation or reduction.

Table 1 shows the reactions which should be considered in the first suppression process involving $CF_3^{\cdot}$ and related species. Reactions 1 and 2 are $CF_3^{\cdot}$-mediated scavenging process of $H^{\cdot}$ and $OH^{\cdot}$. These barrierless and exothermic (ΔH = − 399 and − 486 kJ mol^{-1}, respectively) reactions undoubtedly occur at the burning region.

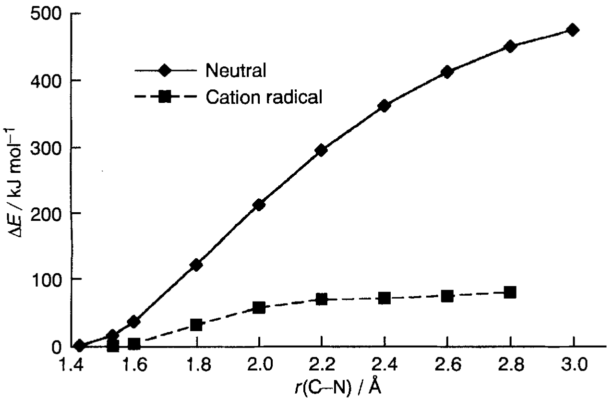
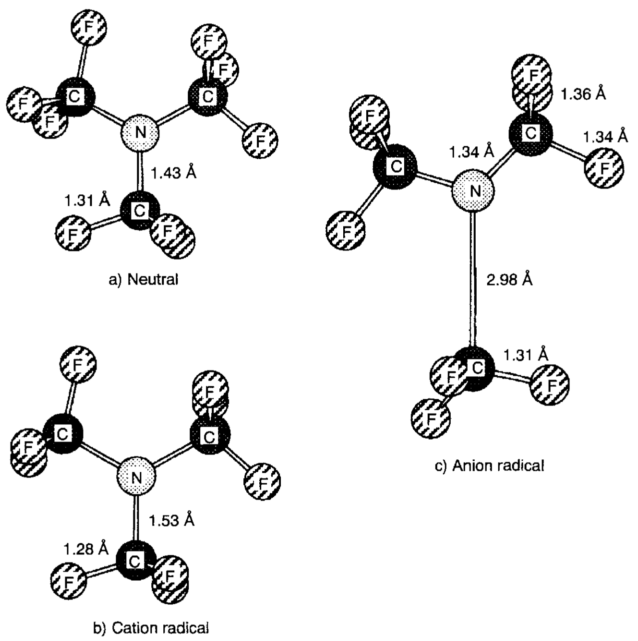


Fig. 1 The C–N bond dissociation energy of perfluorotrimethylamine. Each value is a relative energy of the geometry with an extended one C–N bond against the energy of full optimized geometry (r = 1.43 for neutral and 1.53 Å for cation radical).

Reactions 3, 4 and 5 are the regeneration of $CF_3^{\cdot}$. The activation barrier of reaction 3 is 90 kJ mol^{-1}, and this reaction produces a $CF_3^{\cdot}$ and a H_2 molecule through a small endothermic process of 37 kJ mol^{-1}. Reaction 4 with an activation barrier of 45 kJ mol^{-1} produces $CF_3^{\cdot}$ and a H_2O molecule. Though these two reactions could easily occur in the combustion region, reaction 5 is difficult to activate due to a very high activation energy of 215 kJ mol^{-1}.

Reactions 6, 7 and 8 represent the decomposition of $CF_3^{\cdot}$ and related species. Reaction 6 has no transition state and is endothermic with large ΔH (375 kJ mol^{-1}). This reaction is negligible in comparison with reactions 1 and 2 if the relatively



a) Neutral

b) Cation radical

c) Anion radical

Fig. 2 Optimized structures of perfluorotrimethylamine by GAUSSIAN 92 program with HF/6-31G* basis set

Table 1 Results of *ab initio* molecular orbital calculations[a]

Reaction	ΔE_a[b]/kJ mol^{-1} (lit. value)	ΔH[c]/kJ mol^{-1} (lit. value)
(1) $CF_3^{\cdot} + H^{\cdot} \rightarrow CF_3H$	—[d]	−399
(2) $CF_3^{\cdot} + OH^{\cdot} \rightarrow CF_3OH$	—[d]	−486
(3) $CF_3H + H^{\cdot} \rightarrow CF_3^{\cdot} + H_2$	90	37
(4) $CF_3H + {}^{\cdot}OH \rightarrow CF_3^{\cdot} + H_2O$	45 (16–26)[6,7]	−33 (−54)[7]
(5) $CF_3OH + H^{\cdot} \rightarrow CF_3^{\cdot} + H_2O$	215	55
(6) $CF_3^{\cdot} \rightarrow CF_2{:} + F^{\cdot}$	—[d]	375
(7) $CF_3H \rightarrow CF_2{:} + HF$	336	279
(8) $CF_3OH \rightarrow F_2C = O + HF$[e]	184	51 (~84)[9]

[a] Calculated at the MP2(FU)/6–31G(d) level with zero-point energy correction. The values in the parenthesis are experimental values. [b] Activation energy relative to isolated reactions. [c] Reaction enthalpy calculated by $\Delta H = \Delta E + \Delta(PV) = \Delta E + \Delta nRT$ at 298.15 K. [d] No transition state was found. [e] Higher level calculations were performed by Francisco.[8]

high concentration of H· or OH· is taken into account. Because the activation energy of reaction 7 is as high as 336 kJ mol^{-1}, CF_3H prefers to regenerate $CF_3\cdot$ rather than decompose. However, CF_3OH can decompose into $CF_2 = O + HF$ because the activation energy of reaction 8 (184 kJ mol^{-1}) is comparable to that of reaction 5 (215 kJ mol^{-1}).

We summarize the $CF_3\cdot$-mediated fire suppression mechanism (Fig. 3). The CF_3H-cycle, which consists of the following reactions,

$$CF_3\cdot + H\cdot \rightarrow CF_3H$$

$$CF_3H + H\cdot \rightarrow CF_3\cdot + H_2$$

$$CF_3H + OH\cdot \rightarrow CF_3\cdot + H_2O$$

catalytically converts H· and OH· into relatively unreactive H_2 and H_2O molecules. This cycle is similar to that with the bromine atom so that $CF_3\cdot$ can also suppress fire effectively *via* this cycle. Moreover, there is another CF_3OH cycle which consists of the following reactions.

$$CF_3\cdot + OH\cdot \rightarrow CF_3OH$$

$$CF_3OH + H\cdot \rightarrow CF_3\cdot + H_2O$$

The latter reaction, the regeneration of $CF_3\cdot$, has a large activation energy (215 kJ mol^{-1}) comparable to the one for the following decomposition reaction (184 kJ mol^{-1}).

$$CF_3OH \rightarrow CF_2 = O + HF$$

Therefore, both reactions are in competition. Though some H· or OH· are also consumed in this decomposition, the reaction is less effective as regards fire suppression than the cyclic one (CF_3H-cycle and CF_3OH-cycle) as it is not catalytic.

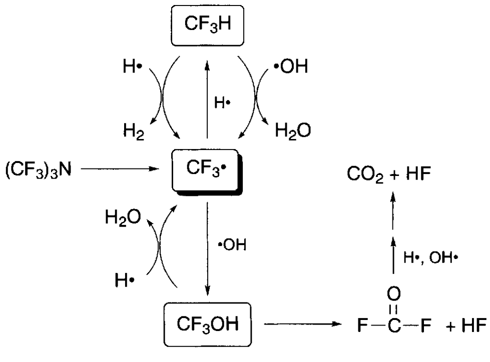


Fig. 3 $CF_3\cdot$-mediated fire suppression mechanism

We thus propose a new mechanism in which $CF_3\cdot$ mimics the fire-extinguishing role played by bromine atoms. According to the proposed mechanism, the compounds having a potential to release large amount of $CF_3\cdot$ and might also be good candidates for use in new fire extinguishers.

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