Experimental Study on Flammability Characteristics of Perfluorocarbons

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ABSTRACT

In the field of fire research, perfluorobutane, which is one of perfluorocarbons, is known as a HALON alternative. On the other hand, perfluorocarbons are known to react with silane. In this case, perfluorobutane is an oxidizer. There is one more different situation. In making fluoro128resin, there sometimes occur explosion incidents. This explosion is considered to occur because gaseous perfluorocarbons, which are by-products of fluororesin, react with fluorine. In this case, perfluorobutane is a fuel. These facts suggest that perfluorocarbon can be a fire suppressant, an oxidizer, or a fuel.

In this study, three types of perfluorocarbon mixture, which are methane/perfluorocarbon/air, silane/perfluorocarbon/nitrogen, and perfluorocarbon/fluorine/nitrogen mixtures, were examined experimentally on their flammability. In the later two mixtures, nitrogen was added as an inert gas. In the three types of mixture, perfluorocarbon was expected to act as a fire suppressant, an oxidizer, and a fuel, respectively. Their flammability areas were revealed quantitatively as triangular flammability diagrams, and the fact that perfluorocarbon suppresses methane/air combustion and reacts with silane or fluorine was ascertained.

KEYWORDS: Perfluorocarbon, Gas Explosion, Explosion Area, Flammability Limit

INTRODUCTION

Recently, many kinds of gas have been used in modern industries such as semiconductor or fine chemical production. There are several gases, which have not been used widely, so their flammability characteristics are not known well. Some gases were studied, and their flammability characteristics were reported already [1,2]. However, there are many gases waiting to be investigated its flammability characteristics. In this study, a series of

perfluorocarbons was studied, because they have very interesting flammability characteristics among remaining gases.

In the field of fire research, perfluorobutane (C_4F_{10}; PFC3-1-10), that is one of perfluorocarbons (C_mF_{2m+2}), is known as a fire-extinguishing agent. On the other hand, as one of semiconductor material gases, halogenated hydrocarbons are known to react with silane. Therefore, C_4F_{10} is also considered to react with silane. In this case, C_4F_{10} is not a fire-extinguishing agent, but an oxidizer. Flammability of each material is relative characteristics. It depends on relative stability of reactants and products. If there were any more stable products than reactants, reaction may occur. In the case of perfluorobutane and silane, methane and tetrafluorosilane (SiF_4) are estimated as products and they are more stable than reactants.

In making fluororesin, there sometimes occurs explosion incident. At an incident, there are gaseous perfluorocarbons and fluorine. Gaseous perfluorocarbons are by-products of fluororesin, and fluorine is reactant to make fluororesin. In the series of C_mF_{2m+2}, tetrafluoromethane (CF_4) is the most stable. It suggests other C_mF_{2m+2} can react with fluorine to produce CF_4. In this case, fluorine is considered an oxidizer.

These facts can be drawn qualitatively from fundamental chemical knowledge, but they are not enough for preventing explosion hazard. These gases must be used together for producing some semiconductors or fluororesins. Quantitative evaluation of their flammability diagram should be done for reducing explosion hazard in such industries.

Then, in this study, flammability diagrams of C_mF_{2m+2} in aforementioned three types of mixtures are evaluated quantitatively, and discussed.

EXPERIMENTS

Experimental Procedure

Experimental apparatus. Figure 1 illustrates overall view of an experimental apparatus. It consists of an explosion vessel, a mixing vessel, a vacuum pump, and piping.

The explosion vessel was made from a stainless steel cylinder. Its inner diameter was 100mm, and height was 100mm. A couple of tungsten spark plugs were set at ca. 50mm above the bottom of the vessel. Pressure history after ignition was measured by a pressure transducer(range:$0 \sim 10$kgf/cm^2, KYOWA PHS-10KA), and recorded by a digital storage oscilloscope (HITACHI VC-6175).

The mixing vessel was made from a stainless steel cylinder with a semispherical bottom. Its inner diameter was 100mm, and height was 150mm. It had a mixing impeller of 1000-rpm mixing ability at inner top. Composition of tested gas mixtures was determined by partial pressure of each component measured by a pressure sensor.
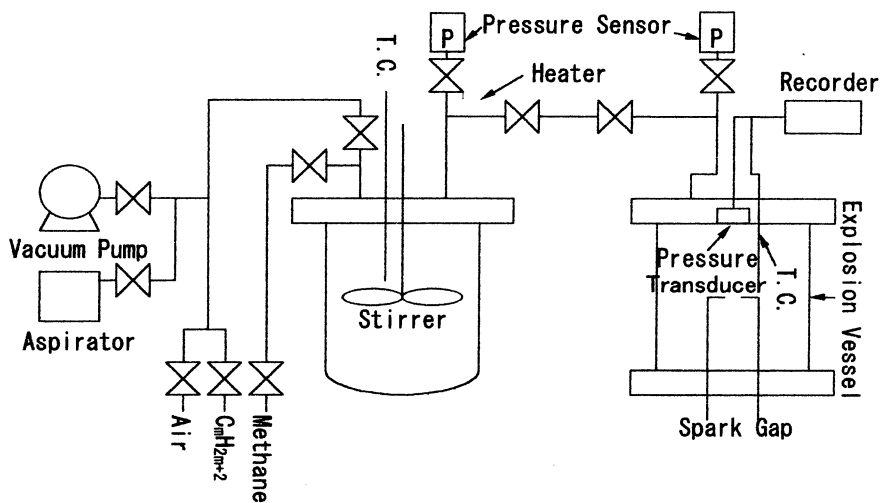
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FIGURE 1 Experimental Apparatus for examining flammability of the first type mixture.

Experimental procedure.   The explosion vessel, the mixing vessel, and piping were vacuumed at first, then each component was introduced into the mixing vessel as each gas had predetermined partial pressure.   Composition of the mixture was determined from partial pressures of each gas.   This mixture was stirred in 5 min by a stirrer.   Then it was transferred to the explosion vessel as the mixture had atmospheric pressure.   The mixture was ignited in the explosion vessel with ignition energy of 300J (15kV, 20mA, 1s) supplied by a neon transformer-type power supply.   Pressure history after ignition was recorded by a digital storage oscilloscope.   Occurrence of explosion was judged from the pressure history: i.e. the maximum pressure exceeded 0.01 MPa or not.

Sample gases.   Three types of mixture were tested.   The first type mixture was composed of methane (CH_4), C_mF_{2m+2} and air.   The second type mixture was composed of silane (SiH_4), C_mF_{2m+2} and nitrogen (N_2).   The third type mixture was C_mF_{2m+2}, fluorine (F_2) and nitrogen.   As C_mF_{2m+2}, perfluoromethane (CF_4), perfluoroethane (C_2F_6), perfluoropropane (C_3F_8), and perfluorobutane (C_4F_{10}) were used for the first type mixture. Perfluoroethane, perfluorobutane, perfluorohexane (C_6F_{14}), and perfluorooctane (C_8F_{18}) were used for the second and the third type mixtures.

Experimental Results

Flammability areas of the first type mixture.   Figure 2 shows flammability areas of the first type mixtures.   First, flammability limits of methane in air that are shown at the vertical line should be compared with literature data [3].   Usually, the flammability range of methane in air is said to be from 5.0 vol% to 15.0 vol%.   However, this figure shows it is wider than
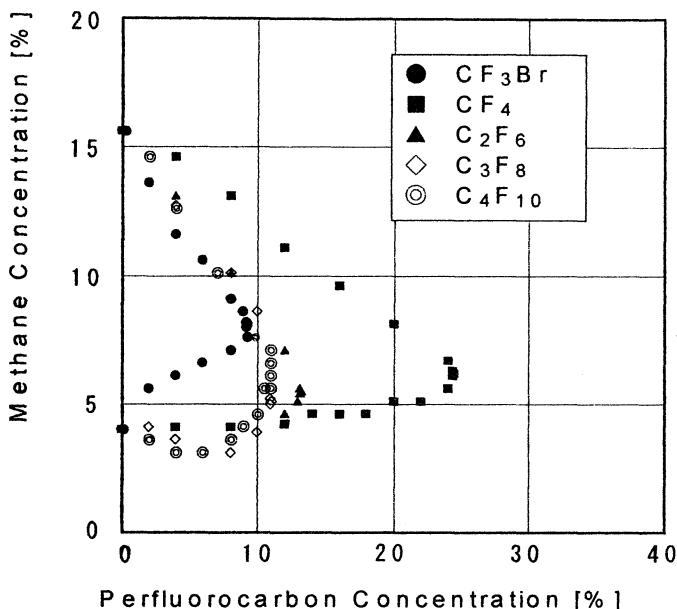
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FIGURE 2 Flammability areas of the first type mixtures. HALON1301 is also plotted as reference.

usual. Lower and higher flammability limits are 4.4 vol% and 16.0 vol%, respectively. Namely, this apparatus gives wider flammable area than the explosion burette system. The difference is considered to come mainly from the higher ignition energy of this apparatus.

So-called peak concentration is concentration of perfluorocarbon at the rightmost point of the flammability area. Halon 1301 (CF_3Br) was also tested and shown in this figure as reference. It has the smallest peak concentration among gases shown in Fig. 2. Observed peak concentration decreases as carbon number increases. However, difference between peak concentration of neighboring perfluorocarbons decreases as increase of carbon number, compared with difference between heat capacity of each gas. Peak concentrations of C_3F_8 and C_4F_{10} are almost identical, and they are close to the peak concentration of Halon 1301. Peak concentration and heat capacity of each perfluorocarbon is summarized in Table 1.

In addition, lower side boundaries of the flammability areas for C_3F_8 and C_4F_{10} are widened toward more fuel lean area. This fact already suggested by Saito et al. [4] for C_4F_{10} and C_3F_7H. However, CF_4 and C_2F_6 showed no such tendency. Cause of these observations will be discussed later.

As mentioned above, Saito et al. observed the flammability area of C_4F_{10}, which is one of the halon replacements called as FC-3-1-10. They used tubular flame burner to form a methane-

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TABLE 1 Peak Concentrations of C_mF_{2m+2} for Methane/ C_mF_{2m+2}/Air mixture.

Suppressant	Heat Capacity $(J \cdot mol^{-1} \cdot K^{-1})$	Peak Concentration
CF_3Br	69.5	9.3
CF_4	61.09	24.5
C_2F_6	105.85	13.2
C_3F_8	144.68	11.1
C_4F_{10}	183.51	11.0

air flame.   Then C_4F_{10} was added until the flame was blown out.   Their apparatus also gave wide flammable range for methane-air mixture, which was from 4.7 vol% to 15.1 vol%.   The peak concentration for C_4F_{10} was 9.4 vol% in their study.   As the difference of the methane-air flammable range, our apparatus gives larger peak concentration than their result.   One of the causes, which cause the difference, is that our apparatus measures limit of ignition, on the other hand, their apparatus measured limit of extinction.

Flammability areas of the second type mixture.   Figure 3 shows triangular flammability diagrams of a) $SiH_4/C_2F_6/N_2$ mixture and b) $SiH_4/C_4F_{10}/N_2$ mixture.   Straight lines in the triangular diagrams show chemical equilibrium for each mixture, which is according to complete combustion reaction discussed later.   It should be noted that scale of the right diagram is four times larger than the left diagram.   The right diagram just shows right
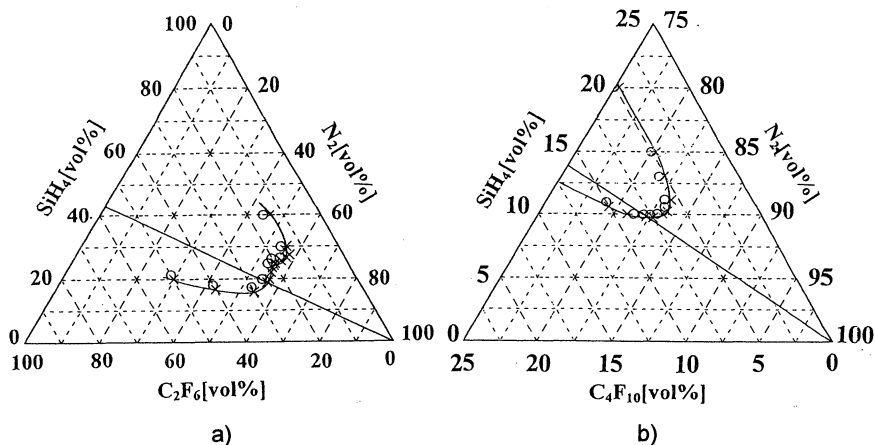

FIGURE 3. Flammability areas of the second type mixture; a) $SiH_4/C_2F_6/N_2$, b) $SiH_4/C_4F_{10}/N_2$

bottom corner of the triangular diagram.

Peak of the flammability area is not clear for the C_2F_6 mixture. It looks like to have two heads. Peak of the flammability area for the C_4F_{10} mixture is rather clear than that for the C_2F_6 mixture.

Although there is a little quantitative difference, flammability areas of C_6F_{14} mixture and C_8F_{18} mixture had almost the same shapes with that of the C_4F_{10} mixture. Peak concentrations and observed lowest concentrations of each component along the flammability area for the $SiH_4/C_mF_{2m+2}/N_2$ mixtures are summarized in Table 2.

TABLE 2 Peak concentrations of N_2 and lowest flammable concentrations of SiH_4 and C_mF_{2m+2} for $SiH_4/C_mF_{2m+2}/N_2$ mixture.

	C_2F_6	C_4F_{10}	C_6F_{14}	C_8F_{18}
Peak concentration of N_2 (vol%)	58	83.8	87.3	87.4
Lowest SiH_4 concentration (vol%)	18	9.8	8.8	9.0
Lowest C_mF_{2m+2} concentration (vol%)	14	4.8	3.0	2.6

Flammability areas of the third type mixture. Figure 4 shows triangular flammability
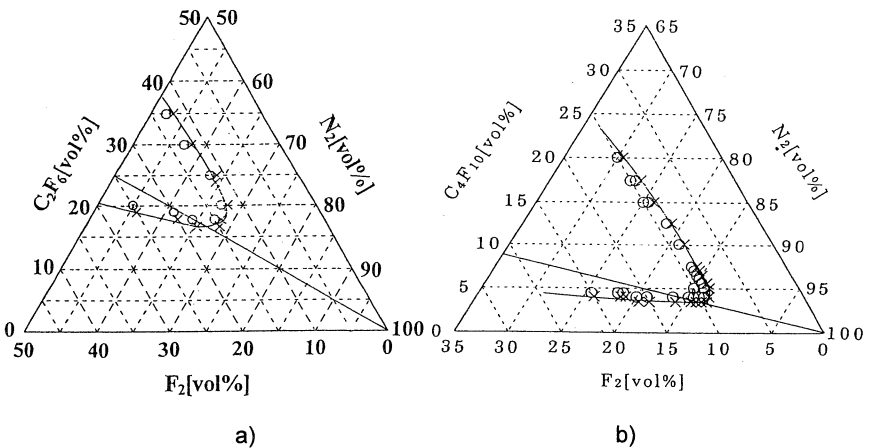

a)   b)

FIGURE 4. Flammability areas of the third type mixture; a) $C_2F_6/F_2/N_2$, b) $C_4F_{10}/F_2/N_2$

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diagrams of a) $C_2F_6/F_2/N_2$ mixture and b) $C_4F_{10}/F_2/N_2$ mixture. Flammability areas for these mixtures have clear triangular shape. Peak concentration can be determined clearly. Similarly with the second type mixture, peak concentration of the C_4F_{10} mixture is much different from that of the C_2F_6 mixture. Flammability area of the C_4F_{10} mixture is wider than that of the C_2F_6 mixture.

Again, compared to the difference between C_2F_6 and C_4F_{10}, flammability diagrams of C_6F_{14} and C_8F_{18} mixtures were close to that of the C_4F_{10} mixture. Peak concentrations and observed lowest concentrations of each component along the flammability area for the $C_mF_{2m+2}/F_2/N_2$ mixtures are summarized in Table 3.

TABLE 3 Peak concentrations of N_2 and lowest flammable concentrations of C_mF_{2m+2} and F_2 for $C_mF_{2m+2}/F_2/N_2$ mixture.

	C_2F_6	C_4F_{10}	C_6F_{14}	C_8F_{18}
Peak concentration of N_2 (vol%)	68	87.0	90.3	91.5
Lowest C_mF_{2m+2} concentration (vol%)	17	3.5	1.8	1.5
Lowest F_2 concentration (vol%)	11	8.5	6.8	6.5

DISCUSSION

Reaction of the first type mixture. Minute reaction scheme of the first type mixture was studied well elsewhere for revealing flame extinction mechanism of halogenated hydrocarbons.
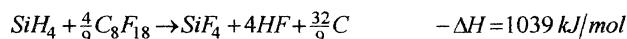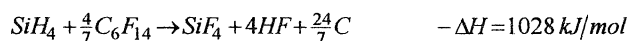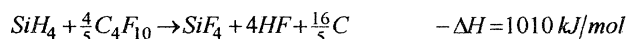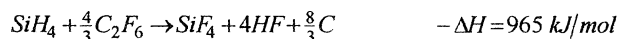
Comparing peak concentrations of perfluorocarbons (CF_4, C_2F_6, C_3F_8, C_4F_{10}), the peak concentration seems to decrease as carbon number increases. In this case, carbon number corresponds with heat capacity. Namely, heat capacity increases with carbon number increases. Therefore, if peak concentration depends only on heat capacity, it should decrease as carbon number increases. However, three perfluorocarbons except CF_4 have comparable peak concentrations (11-13%). Nevertheless C_4F_{10} has 80 % larger heat capacity than C_2F_6, difference in the peak concentration is only about 20%. It means that their fire suppression mechanism is affected not only by heat-sink effect but also by chemical effect. Radical scavenging of CF_3 radical is considered the main chemical effect for fluorohydrocarbons [5,6] These three perfluorocarbons have two CF_3 groups each in one molecule, so they have almost the same fire suppression ability except difference in heat sink effect.

This was more clear at 200°C. The explosion vessel identical with the present study was placed in a temperature controlled oven, which could hold the vessel up to 200°C. Measurement of the peak concentrations was done by using the vessel. Observed peak concentrations of perfluorocarbons (CF_4, C_2F_6, C_3F_8, C_4F_{10}) were 26.0 vol%, 14.6 vol%, 14.2 vol%, 14.1 vol%, respectively [7]. Peak concentrations of perfluorocarbons with two

CF_3 groups were much closer at elevated temperature. In addition, peak concentration of Halon 1301 was 14.1 vol% at $200\,^\circ C$. Difference of peak concentrations between perfluorocarbons and Halon 1301 was little.

As seen in Fig. 2, in the case of C_3F_8 and C_4F_{10}, their flammability areas are widened toward fuel lean area. However, such a fact was not observed in the case of CF_4 and C_2F_6. These show C_3F_8 and C_4F_{10} are a little flammable even in air. They release carbon atoms when they decompose, so released carbon atoms show inflammability.

<u>Reaction of the second type mixture.</u> Reaction equations of the second type mixtures are estimated as follows by using computer program CHETAH [8], which conducts thermodynamic calculation.

$$SiH_4 + \tfrac{4}{3}C_2F_6 \rightarrow SiF_4 + 4HF + \tfrac{8}{3}C \qquad -\Delta H = 965\,kJ/mol$$

$$SiH_4 + \tfrac{4}{5}C_4F_{10} \rightarrow SiF_4 + 4HF + \tfrac{16}{5}C \qquad -\Delta H = 1010\,kJ/mol$$

$$SiH_4 + \tfrac{4}{7}C_6F_{14} \rightarrow SiF_4 + 4HF + \tfrac{24}{7}C \qquad -\Delta H = 1028\,kJ/mol$$

$$SiH_4 + \tfrac{4}{9}C_8F_{18} \rightarrow SiF_4 + 4HF + \tfrac{32}{9}C \qquad -\Delta H = 1039\,kJ/mol$$

These reaction equations were ascertained indirectly by facts that there remained carbon deposit in the explosion vessel after explosion, and peaks of their flammability areas are close to the lines showing stoichiometry for the reaction equations.

Heat of combustion of methane is 890.3 kJ/mol as reference. Comparing the above heats of reaction with that for methane combustion, these reactions are worse to be named as combustion.

These large heats of reaction are related with differences in heats of formation between reactants and products. Related bond energies are Si-H(319kJ/mol), C-F(484kJ/mol), Si-F(592kJ/mol), H-F(567 kJ/mol), and C-H(411kJ/mol). Namely, Si is more stable when it combines with F than H, and F is more stable when it combines with H than C. Therefore, the products are expected from the reactants. .

Adiabatic flame temperatures at boundaries of the flammability area for the second type mixtures were calculated by using Gibb's free energy. The adiabatic flame temperatures for C_4F_{10}, C_6F_{14}, and C_8F_{18} mixtures are all 1500 K. However, the adiabatic temperature for C_2F_6 mixture is 1800 K. The difference of the adiabatic flame temperatures comes from difference in C-C bond energy between C_2F_6 and others. Namely, bond dissociation energy of CF_3-CF_3 bond(410kJ/mol) is larger than other normal C-C bond(354kJ/mol).

<u>Reaction of the third type mixture.</u> Reaction equations of the third type mixtures are estimated as follows.

$$C_2F_6 + F_2 \rightarrow 2CF_4 \qquad -\Delta H = 523.1\,kJ/mol$$

$$C_4F_{10} + 3F_2 \rightarrow 4CF_4 \qquad -\Delta H = 1573\,kJ/mol$$

$$C_6F_{14} + 5F_2 \rightarrow 6CF_4 \qquad -\Delta H = 2622 \ kJ/mol$$
$$C_8F_{18} + 7F_2 \rightarrow 8CF_4 \qquad -\Delta H = 3672 \ kJ/mol$$

Comparing the above heats of reaction with that for methane combustion, heat of C_2F_6 and F_2 reaction is a little smaller than methane combustion. However, they are large enough to be named as combustion.

As mentioned above, these large heats of reaction are related with differences of heats of formation between reactants and products. Related bond energies are C-F(484kJ/mol), C-C(344kJ/mol) and F-F(155kJ/mol). Namely, C is more stable when it combines with F than other C, and F is more stable when it combines with C than F. Therefore, the above reaction equations are derived.

Considering bond energy of F compound, total bond energy of HF is larger than H_2O. Similarly, total bond energy of CF_4 is larger than CO_2. Therefore, H_2O and CO_2 can react with F_2. In other words, H_2O and CO_2 can burn in F_2 atmosphere. There is no quantitative data, but water drop is known to burn in ClF_3 atmosphere, which is a little weak fluorination agent than F_2.

Adiabatic flame temperatures at boundaries of the flammability area for the third type mixtures were also calculated. The adiabatic flame temperatures at fluorine-rich side boundaries for C_4F_{10}, C_6F_{14}, and C_8F_{18} mixtures are all 1700 K. The adiabatic temperature for C_2F_6 mixture is 2100 K. There is again difference in the adiabatic flame temperatures. It also comes from difference in C-C bond energy between C_2F_6 and others. The adiabatic flame temperature at fluorine-lean side boundary is about 850 K, but it fluctuates much along the boundary.

CONCLUSION

Flammability characteristics of perfluorocarbon were examined experimentally in this study. Perfluorocarbon was revealed to act as a fire suppressant in methane/perfluorocarbon/air mixture, as an oxidizer in silane/perfluorocarbon/nitrogen mixture, or as a fuel in perfluorocarbon/fluorine/nitrogen mixture. Their flammability diagrams and peak concentrations were obtained quantitatively.

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