

Review

Alternative Environmentally Friendly Insulating Gases for SF₆

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Received: 12 March 2019; Accepted: 8 April 2019; Published: 15 April 2019



Abstract: Sulfur hexafluoride (SF₆) shows excellent insulation performance as an insulating gas. It is suitable for various climate conditions due to its low boiling point (−64 °C). Therefore, it has been widely used in power grid equipment. However, its global warming potential (GWP) is 23,500 times higher than that of CO₂. Thus, it is imperative to find an environmentally friendly insulating gas with excellent insulation performance, lower GWP, and which is harmless to equipment and workers to replace SF₆. In this review, four possible alternatives, including perfluorocarbons, trifluoroiodomethane, perfluorinated ketones, and fluoronitrile are reviewed in terms of basic physicochemical properties, insulation properties, decomposition properties, and compatibility with metals. The influences of trace H₂O or O₂ on their insulation performances are also discussed. The insulation strengths of these insulating gases were comparable to or higher than that of SF₆. The GWPs of these insulating gases were lower than that of SF₆. Due to their relatively high boiling point, they should be used as a mixture with buffering gases with low boiling points. Based on these four characteristics, perfluorinated ketones (C₅F₁₀O and C₆F₁₂O) and fluoronitrile (C₄F₇N) could partially substitute SF₆ in some electrical equipment. Finally, some future needs and perspectives of environmentally friendly insulating gases are addressed for further studies.

Keywords: SF₆; environmentally friendly insulating gas; perfluorocarbon; trifluoroiodomethane; perfluorinated ketone; fluoronitrile

1. Introduction

In high-voltage transmission systems, gas insulation has the advantages of being light weight, cost-effective, having simple manufacturing construction, and recyclability when compared with liquid or solid insulation. Thus, it has been widely applied in power grids all over the world. At first, a mixture of CCl₄ vapor and air was used as insulating gas. Herb and Rodine found that CCl₄ vapor and air can synergize and enhance the dielectric strength, especially with a lower CCl₄ concentration [1]. Charlton and Cooper found that CCl₂F₂ and CF₄ also showed better dielectric strength than N₂ [2,3]. SF₆ was first patented as an insulating gas by Cooper in 1938 (Figure 1). Since then, it has been studied systematically. It has been noted for its arc quenching capability and insulating properties. The excellent arc quenching capability is because of its high heat capacity, dissociation, and reassembly properties. The high dielectric strength can be attributed to its large molecular weight, complexity, and electron affinity, which affects the reaction between gas molecules and free electrons [4]. The decomposed products of SF₆ can recombine again when the temperature decreases, which ensures that the insulation strength is maintained well. As a result, it decomposes by only about 5% after working at 140 °C for 25 years [5]. Besides, it is non-poisonous, chemically stable, and non-flammable, which provides security for operation in practical applications. Considering the dielectric strength, cost, stability,

toxicity, and liquefaction temperature, SF₆ stands out as the best insulating gas. It has been widely used in air-insulated switchgear (AIS) and gas-insulated switchgear (GIS) since the 1960s [6].

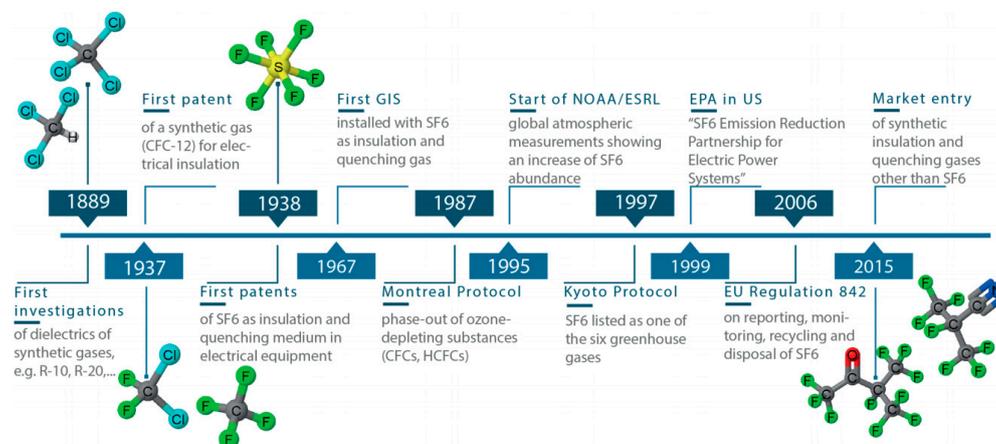


Figure 1. Development of insulating gases [7].

However, SF₆ has also caused serious environmental problems. It was identified as one of the seven greenhouse gases in the Kyoto Protocol. It shows a remarkable absorption at infrared frequency and absorbs upward radiance 42,000 times more effectively than CO₂, thus causing a great greenhouse effect [7]. The global warming potential (GWP) of SF₆ is 23,500 times higher than that of CO₂ over a 100 year integration time horizon according to the report of Intergovernmental Panel on Climate Change (IPCC) in 2013, and its lifetime in the atmosphere reached to 850 years with an uncertainty range of 580–1400 years [8]. With the rapid development of electrical insulation media, large amounts of SF₆ have been leaking or discharged into the atmosphere. In fact, the concentration of SF₆ in the atmosphere increased by 20% from 2010 to 2015 (Figure 2) [9]. It was estimated that the emissions will reach 4270 ± 1020 t in 2020 [10]. The greenhouse effect caused by SF₆ will be incalculable. Besides, when water vapor exists in the insulating equipment containing SF₆, the reaction generates SOF₄, SO₂F₂, S₂F₁₀, SF₄, HF, and SO₂. Among the products, SO₂F₂, S₂F₁₀, and SF₄ are highly toxic. HF and SO₂ are corrosive for insulating equipment [11]. Thus, the use and emission of SF₆ should be seriously restricted. One approach to reduce the emission of SF₆ was to replace some of the SF₆ with other inert substances with lower GWPs. For example, SF₆/N₂ was selected. Although the dosage of SF₆ is decreased, the GWP of a SF₆(10%)/N₂ mixture by volume is still unacceptable, at 8650 [9].

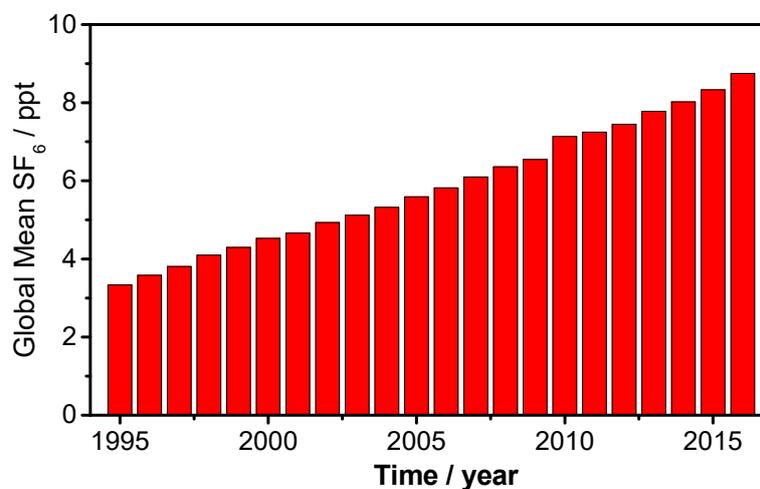


Figure 2. The concentration of SF₆ in the atmosphere since 1995.

Therefore, an environmental alternative to completely replace SF₆ is necessary and urgent. It should meet the features of low GWP, no ozone depletion potential (ODP), it should be non-toxic or hypotoxic, and have high dielectric strength, good thermal conductivity, low boiling point, good compatibility with switchgear materials, etc. [5,9]. Herein, we have reviewed the pioneered studies about environmentally friendly insulating gases, including perfluorocarbon, trifluoriodomethane, perfluorinated ketones, and fluoronitrile (Table 1). For each alternative, its basic physicochemical properties, insulation properties, decomposition properties, metal compatibility, and influence of trace H₂O or O₂ on its insulation performance are reviewed in detail in order to provide a better understanding of these compounds' insulation performances.

Table 1. Basic properties of compounds used in electrical insulation. GWP: global warming potential; ODP: ozone depletion potential.

Chemical Formula	GWP/100-Years	Lifetime/Years	Dielectric Strength Relative to SF ₆	Boiling Point/°C	Toxicity	ODP	Flammability
SF ₆	22,800	850	1	−64	Non-toxic	0	Non-flammable
CF ₄	9200	50,000	0.4	−128	Low-toxicity	0	Non-flammable
C ₂ F ₆	12,200	10,000	0.76	−78.1	Non-toxic	0	Non-flammable
C ₃ F ₈	8830	2600	1.01	−36.7	Non-toxic	0	Non-flammable
c-C ₄ F ₈	8700	3200	1.3	−8	Non-toxic	0	Non-flammable
CF ₃ I	0.4	0.0055	1.23	−22	Non-toxic	0	Non-flammable
C ₅ F ₁₀ O	1	0.044	1.5–2	27	Non-toxic	0	Non-flammable
C ₆ F ₁₂ O	1	0.014	2.7	49	Non-toxic	0	Non-flammable
C ₄ F ₇ N	2100	22	2	−4.7	Non-toxic	0	Non-flammable
CF ₄	6630	50,000	0.4	−128	-	-	Non-flammable
CO ₂	1	-	0.32–0.37	−79	Non-toxic	0	Non-flammable
N ₂	-	-	0.34–0.43	−196	Non-toxic	0	Non-flammable
air	-	-	0.37–0.40	−193	Non-toxic	0	Non-flammable
He	-	-	0.02–0.06	−268.9	Non-toxic	0	Non-flammable
Ar	-	-	0.04–0.10	−186	Non-toxic	0	Non-flammable

2. Perfluorocarbons

Due to the electronegativity of fluorine, it is believed that perfluorocarbon has good insulation performance. Therefore, perfluorocarbons have attracted a great deal of attention as new insulation gases. The mainly proposed perfluorocarbons are CF₄, C₂F₆, C₃F₈, and C₄F₈. Their basic properties are listed in Table 1. Their GWPs are all lower than that of SF₆, they show no ozone depletion potential, comparable dielectric strength, and relatively lower GWPs relative to SF₆.

2.1. Perfluoromethane (CF₄), Perfluoroethane (C₂F₆), and Perfluoropropane (C₃F₈)

CF₄, C₂F₆, and C₃F₈ have the potential to be used in gas insulation equipment because of their strong electronegative property. However, the lifetimes of CF₄ and C₂F₆ are as long as 50,000 and 10,000 years, respectively. Their dielectric strengths are both lower than that of SF₆. Further, CF₄ may cause choking disease. Therefore, CF₄ and C₂F₆ are unsuitable for gas insulation.

Meanwhile, C₃F₈ is harmless to O₃ in the stratosphere. It also has low toxicity, good thermal stability, relatively low boiling point, and comparable dielectric strength to SF₆. The GWP of C₃F₈ is 8830, which is 38.7% that of SF₆. The breakdown voltages of C₃F₈/N₂ or C₃F₈/CO₂ have a significant linear correlation with the ratio of C₃F₈. The GWPs of C₃F₈ (12%)/N₂ (2736) and C₃F₈ (12%)/CO₂ (6612) were found to be 12% and 29% of that of SF₆ (22,800), respectively [12]. The C₃F₈/N₂ mixture exhibited higher dielectric strength than that of C₃F₈/CO₂. When the ratio of C₃F₈ was 20%, the insulation strength of C₃F₈/N₂ reached 60% of that of pure C₃F₈. The insulation strength under 0.79 MPa was comparable to that of SF₆ at 0.5 MPa. Besides, the liquefaction temperature decreased to −30 °C and the GWP also decreased greatly [13]. Thus, it is feasible to apply C₃F₈/N₂ or C₃F₈/CO₂ in practical insulation equipment.

2.2. Perfluorocyclobutane (*c*-C₄F₈)

Among CF₄, C₂F₆, C₃F₈, and *c*-C₄F₈, *c*-C₄F₈ exhibits the highest dielectric strength [14]. The insulation strength is about 1.3 times higher than that of SF₆. The GWP of *c*-C₄F₈ is 8700, which is 38.2% of that of SF₆. Moreover, *c*-C₄F₈ also has the features of non-toxicity, no O₃ destruction, and high thermal stability. Thus, it has the potential to replace SF₆ as an environmentally friendly insulating gas [15]. However, due to its high boiling point (−8 °C), it should be used by mixing with CF₄, N₂, CO₂, or air. The dielectric strength of *c*-C₄F₈/CO₂ is higher than that of SF₆/CO₂, and the GWP of *c*-C₄F₈/CO₂ is much lower than that of SF₆/CO₂ [16]. Li et al. [17] studied the dielectric strength of *c*-C₄F₈ with CF₄, CO₂, N₂, O₂, and air mixture by Boltzmann equation. They found that *c*-C₄F₈/N₂ and *c*-C₄F₈/air mixtures showed comparable dielectric strength, which were higher than those of *c*-C₄F₈/CF₄, *c*-C₄F₈/CO₂, and *c*-C₄F₈/O₂. When the concentration of *c*-C₄F₈ exceeded 80%, the dielectric strengths of *c*-C₄F₈/N₂ and *c*-C₄F₈/air were comparable to that of pure SF₆. After 30 experimental breakdown tests, the breakdown voltage of the *c*-C₄F₈/N₂ decreased by only 0.76%, indicating a good self-recovery characteristic. It was also reported that the decomposition rate of *c*-C₄F₈/N₂ was lower than that of pure *c*-C₄F₈ at the same temperature, which is more suitable in practical gas insulation systems. The main decomposition path of *c*-C₄F₈ was from *c*-C₄F₈ to C₂F₄, and it further decomposed into CF₂, F, CF₃, CF, C, CF₄, and C₂F₄ [18]. However, when a certain amount of O₂ was added into the mixture gas of *c*-C₄F₈/N₂, the breakdown voltage decreased more and more observably with the O₂ content increase from 0% to 1%. Then, the breakdown voltage decreased slightly when further increase of the O₂ content. The breakdown voltage decreased by 4.47% after 30 breakdown tests in the presence of 3% O₂. This was mainly attributed to the relatively lower dielectric strength of O₂ and the new produced products [19]. O₂ promotes the decomposition of *c*-C₄F₈ and generates the very toxic and corrosive COF₂. Thus *c*-C₄F₈ should be used without O₂ [20].

3. Trifluoroiodomethane (CF₃I)

CF₃I is a colorless, odorless, incombustible, and stable gas. Because of the excellent electronegative property of CF₃I, its dielectric strength is 1.2 times higher than that of SF₆. Besides, the GWP of CF₃I is 1–5, which is far less than that of SF₆. The C–I bond can be easily cracked under UV irradiation. Therefore, its lifetime in atmosphere is less than 2 days, and it does not cause O₃ destruction [21,22]. According to these characteristics, CF₃I has been a potential alternative to SF₆ as a new insulating gas.

Due to its high boiling point of −22.5 °C and the formation of I₂ in pure CF₃I, CF₃I should be mixed with other gases with low boiling point, such as N₂, CO₂, O₂, air, CF₄, Ar, Xe, and He. Among the mixtures, CF₃I/N₂ showed the best insulating strength [22,23]. Li et al. [22] found that the saturated vapor pressure of CF₃I/N₂ was higher than that of *c*-C₄F₈/N₂, indicating that CF₃I–N₂ can be used under higher pressure. Besides, the dielectric strength of CF₃I/N₂ was higher than that of *c*-C₄F₈/N₂, and they were both higher than that of SF₆/N₂ [24]. The dielectric strength of CF₃I (20%)/N₂ at 0.79 MPa was 102% of SF₆ at 0.5 MPa at −10 °C. When the CF₃I concentration exceeded 65%, the insulation strength of CF₃I/N₂ was higher than that of SF₆/N₂. It was even higher than that of pure SF₆ when CF₃I concentration exceeded 70% [23]. Regarding CF₃I/CO₂, the CF₃I and CO₂ can act synergistically and enhance the physicochemical properties of CF₃I. When the ratio of CF₃I or SF₆ was 10%–30% at 0.1–0.3 MPa, the partial discharge inception voltage of CF₃I/CO₂ was 0%–20% higher than that of SF₆/CO₂. The insulation strength of CF₃I/CO₂ was comparable or even higher than that of SF₆/CO₂ [25]. In this case, both the boiling point and insulation strength could satisfy the practical requirements. The breakdown performance of CF₃I/CO₂ was also superior to that of CF₃I/N₂. In quasi-uniform and highly non-uniform electric fields, the breakdown voltages of CF₃I/CO₂ were 84% and 65% of pure SF₆, which were both higher than that of CF₃I/N₂ [26,27]. The 50% breakdown voltages of CF₃I (30%)/CO₂ and CF₃I (20%)/CO₂ under 0.1 MPa were 67.1 and 66.6 kV, respectively. For CF₃I (30%)/N₂ and CF₃I (20%)/N₂, they were 60.5 and 50.1 kV, respectively [28]. After 20 breakdown experiments, less CF₃I decomposed in CF₃I/CO₂ mixture than that in CF₃I/N₂ mixture. It was explained that CO₂ could

provide an additional C source for the reaction system to maintain the C balance, which suppressed the decomposition of CF_3I [26].

According to density functional theory (DFT), the reactions of CF_3I to CF_4 , C_2F_6 , C_2F_4 , and $\text{C}_2\text{F}_5\text{I}$ were more energetically favorable than that to C_3F_8 , C_3F_6 , and I_2 . Thus, the decomposition products were mainly C_2F_6 , C_2F_4 , and I_2 . It can be clearly seen that the transparent glass changed to tawny after several experiments, indicating the formation of I_2 . The products in partial discharge were stable after 20 h test [29]. Although the products cannot reassemble to CF_3I completely after discharge, there is a dynamic equilibrium among CF_3 , CF_2 , I , F , and CF_3I . Thus, the insulating strength can be maintained well for pure CF_3I [30].

However, in the presence of O_2 , the $\text{O}\cdot$ from O_2 consumes free radicals (CF_3 , $\text{CF}_2\cdot$) from CF_3I and generates COF_2 (Figure 3), which is a highly toxic irritant for respiratory mucosa and skin. What is more, it destroys the dynamic equilibrium among CF_3 , CF_2 , I , F , and CF_3I , hindering the regeneration of CF_3I . As a result, the CF_3I content and insulation performance decreased with the extension of discharge time [31]. In order to ensure the insulation strength and safety, the O_2 content in CF_3I cannot exceed 7% and 20%, respectively [32]. Therefore, it is impracticable to use O_2 and air as buffer gases with CF_3I in GIS.

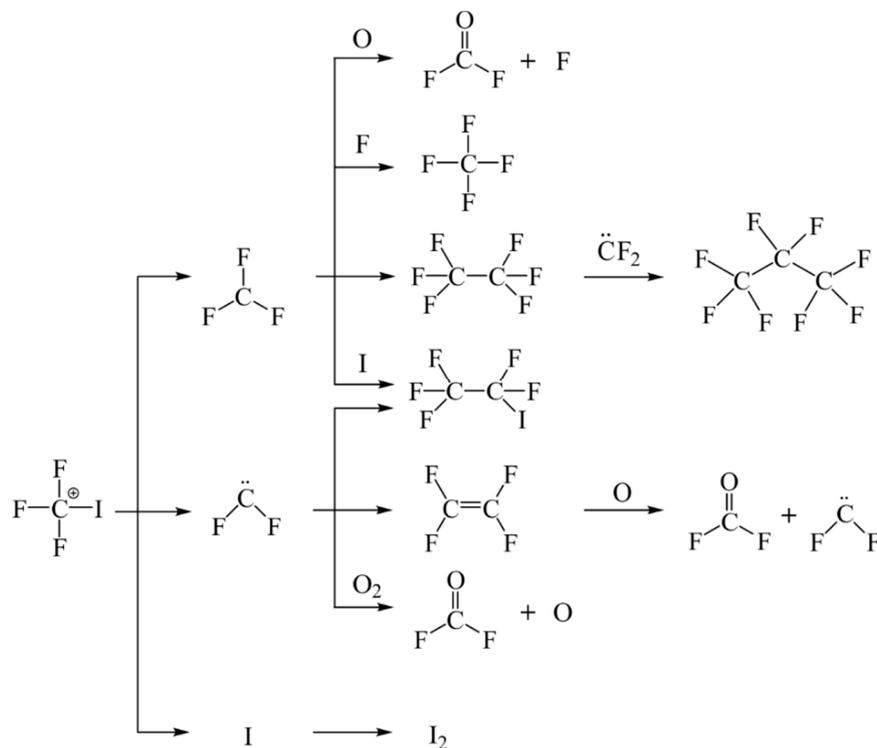


Figure 3. Decomposition mechanism of CH_3I with O_2 during discharge.

Moreover, the free radicals $\text{H}\cdot$ and HO produced from H_2O destroy the balance between CF_3I and free radicals, which aggravates the decomposition of CF_3I and generated C_2F_6 , I_2 , C_2F_4 , $\text{C}_2\text{F}_5\text{I}$, C_3F_8 , HF , H_2 , COF_2 , CF_3H , CF_3OH . As a result, the partial discharge initial voltage and insulating strength decrease gradually [33,34]. So, it is vital to control the content of H_2O in insulating systems.

Zhang et al. [35] studied the influence of metal particles (Cu , Al , and Fe) on the insulation property of CF_3I . They found the metal particles—especially Cu and Al —could increase the electrical conductivity and decrease the insulation strength of CF_3I . The breakdown voltages decreased with the increase of metal particles. Therefore, the metal particles in insulation equipment should be well-covered by an insulating varnish or sleeve to avoid the interaction between CF_3I and metal particles.

Zhang et al. [36] studied the feasibility of $\text{CF}_3\text{I}/\text{N}_2$ in gas insulating equipment. They concluded that CF_3I (30%)/ N_2 at 0.3 MPa could be applied in some low-pressure insulating equipment. By increasing

the total pressure or the partial pressure of CF_3I , the $\text{CF}_3\text{I}/\text{N}_2$ can also be applied in apparatuses requiring high insulation strength. Tan et al. [37] applied a CF_3I (20%)/ N_2 mixture in 126 kV GIL (gas-insulated line). The insulation performance was 83% of that of SF_6 (20%)/ N_2 and 59% of that of pure SF_6 . When the pressure of CF_3I (20%)/ N_2 exceeded 0.7 MPa, it could meet the insulating and safety requirements. However, authors did not consider the safety and feasibility over a long time period.

4. Perfluorinated Ketones ($\text{C}_5\text{F}_{10}\text{O}$ and $\text{C}_6\text{F}_{12}\text{O}$)

Recently, it was found that perfluorinated ketones ($\text{C}_n\text{F}_{2n}\text{O}$: $\text{C}_5\text{F}_{10}\text{O}$ and $\text{C}_6\text{F}_{12}\text{O}$) can act as new eco-friendly and promising insulating gases. They were initially applied in fire extinguishing applications due to their incombustibility [38,39]. Their physical property parameters can be seen in Table 1. $\text{C}_n\text{F}_{2n}\text{O}$ shows high insulation capacity and its dielectric strength is 1–3 times higher than that of SF_6 . Moreover, the atmospheric lifetime is just 7 days because of its instability under UV radiation, and it does not cause any damage to O_3 . Therefore, it causes low greenhouse effect and other atmospheric environmental damage. However, the boiling point of $\text{C}_n\text{F}_{2n}\text{O}$ ($n = 5, 6$) is above 27°C , making it easy to liquify under natural conditions. Therefore, it is infeasible to apply pure fluoroketones as insulating gases, but only as additives to other buffer gases with low boiling points, such as N_2 , air, and CO_2 .

4.1. Perfluoropentanone ($\text{C}_5\text{F}_{10}\text{O}$)

Zhang et al. [40,41] studied the decomposition mechanism of $\text{C}_5\text{F}_{10}\text{O}$ products by gas chromatography-mass spectrometry (GC-MS) and density functional theory (DFT). The reaction paths of $\text{C}_5\text{F}_{10}\text{O}$ are shown in Figure 4. According to the relative energy change, the breakage of the C–C bond between carbonyl carbon and α -carbon atom was more likely to occur and generate $\text{CF}_3\text{CO}\cdot$ and C_3F_7 (Reaction A1) or $\text{C}_3\text{F}_7\text{CO}$ and CF_3 (Reaction B1). They reacted further to generate CF_4 , C_2F_6 , C_3F_8 , C_3F_6 , C_4F_{10} , C_5F_{12} , and C_6F_{14} . The decomposition rate increased with the increase of breakdown tests, generating more products with weaker dielectric strength relative to $\text{C}_5\text{F}_{10}\text{O}$. The products cannot reassemble into $\text{C}_5\text{F}_{10}\text{O}$ when the environment temperature cools down [42]. As a result, the breakdown voltage decreased gradually. Besides, they also found that when the temperature was over 625 K and 825 K, the decomposition of $\text{C}_3\text{F}_7\text{CO}\cdot$ and $\text{CF}_3\text{CO}\cdot$ was enhanced. Reactions A1 and B1 would change to spontaneous. Among the products, C_2F_6 , C_3F_6 , and C_4F_8 have choking, bronchitis, anesthetic, and pneumonia effect. However, the content of $\text{C}_5\text{F}_{10}\text{O}$ in practical application is below 20% and the concentration of products is extremely low. It has been reported that during arc discharge, the product of C_3F_6 was 50 ppm and just 6.5 ppb may have leaked into the air, which was far less than the exposure threshold of 0.1 ppm [43]. Although the GWPs of CF_4 , C_2F_6 , C_3F_8 , C_4F_{10} , and C_6F_{14} are 7390, 12,200, 8830, 8860, and 9300 (much higher than that of $\text{C}_5\text{F}_{10}\text{O}$), it should be noted that the concentration of deposited products is extremely low under normal working conditions [44]. Therefore, $\text{C}_5\text{F}_{10}\text{O}$ is safe as an insulating gas. The application in GIS does not pose a threat to the environment or human health.

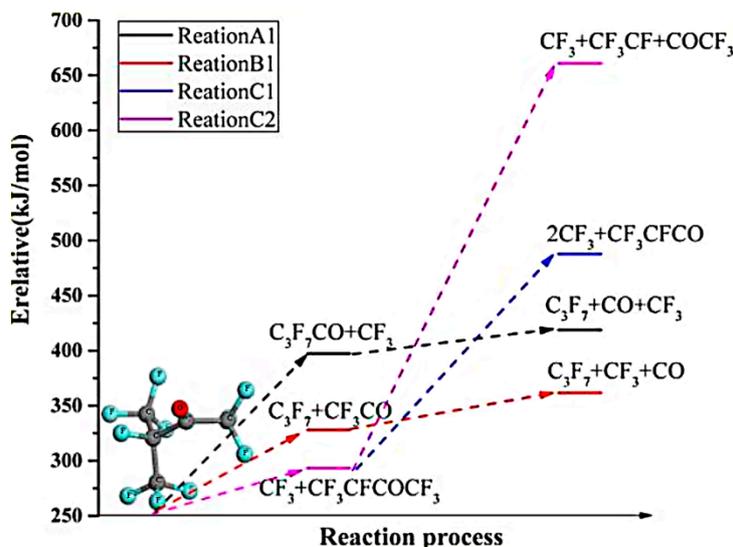


Figure 4. The main reaction paths of $C_5F_{10}O$ [40].

As an additive, the ratio of $C_5F_{10}O$ in mixtures is usually less than 20%. For $C_5F_{10}O/N_2$ mixtures, the GWPs are lower than 0.7. However, these mixtures generate some CO and CF_3CN with high toxicity. For $C_5F_{10}O/air$ mixtures, less CO was generated and more oxygenated chemicals were generated, decreasing the toxicity of the products. However, more $C_5F_{10}O$ would decompose in $C_5F_{10}O/air$ mixtures than that in $C_5F_{10}O/N_2$ mixtures [45]. For $C_5F_{10}O/CO_2$ mixtures, the breakdown voltages of $C_5F_{10}O$ (10%)/ CO_2 mixtures can reach to 62% of SF_6 under 200 kPa. When the percentage of $C_5F_{10}O$ increased to 20%, the breakdown voltage increased by 32.5% [46].

Zhang et al. [47] studied the compatibility between $C_5F_{10}O$ and Cu by theoretical calculation. Due to the high activity of the carbonyl group in $C_5F_{10}O$, it could be strongly absorbed on Cu (1 1 1) surfaces by chemical bonding. However, the interaction between the F atom and Cu is weak, which contributed to physical adsorption. Besides, they studied the compatibility between $C_5F_{10}O$ and Al or Ag. The strong interaction between $C_5F_{10}O$ and Al (1 1 1) was chemical adsorption. The weak adsorption on Ag (1 1 1) resulted from van der Waals force. Thus, they considered that Ag is more compatible with $C_5F_{10}O$ than Cu and Al [48].

4.2. Perfluorohexanone($C_6F_{12}O$)

When adding 3% $C_6F_{12}O$ into N_2 , the liquefaction temperature was $-26\text{ }^\circ\text{C}$. The breakdown voltage of the mixture gas was 1.7 times higher than that of the pure N_2 , which was equal to that of SF_6 (10%)/ N_2 . The decomposed products of $C_6F_{12}O/N_2$ were mainly CO, CO_2 , CF_4 , C_2F_6 , C_2F_4 , C_3F_8 , C_3F_6 , CF_3CN , C_2HF_5 , C_4F_{10} , C_5F_{12} , and C_6F_{14} . Similar to $C_5F_{10}O/N_2$, the reaction generated CF_3CN , which causes mortal danger [49]. Besides, the products (e.g., C_2F_6 , C_3F_8 , and C_4F_{10}) showed high insulation strength. Thus, the breakdown voltage of $C_6F_{12}O$ (3%)/ N_2 was maintained even after 100 voltage breakdown tests. With the increase of total pressure, the breakdown voltage of the mixture gas decreased gradually [50,51]. For the mixture of $C_6F_{12}O$ and air, the generation of CF_3CN is avoided. The products are mainly CO_2 , CF_4 , C_2F_6 , C_3F_8 , and $C_2O_3F_6$, among which the content of CO_2 is the highest [49]. When the temperature exceeded $475\text{ }^\circ\text{C}$, the decomposition of $C_6F_{12}O/CO_2$ was enhanced. The possible decomposition paths are shown in Figure 5. The strength of the C–C bond is weaker than that of C–F and C=O bonds. Thus, $C_6F_{12}O$ firstly decomposed into $C_3F_7COCF_2$ and $C_2F_5COCF_2CF_3$. Then, they further decomposed into fragments such as F, $CF_3\cdot$, CF_2 , $CF\cdot$, $C_3F_7\cdot$, CO, COF_2 , and C. These free radicals cannot recombine to $C_6F_{12}O$. The final products were mainly CF_4 , C_2F_6 , C_3F_8 , C_3F_6 , and C_5F_{12} and their contents decreased as follows: $C_2F_6 > C_3F_6 > C_3F_8 > CF_4$ [52].

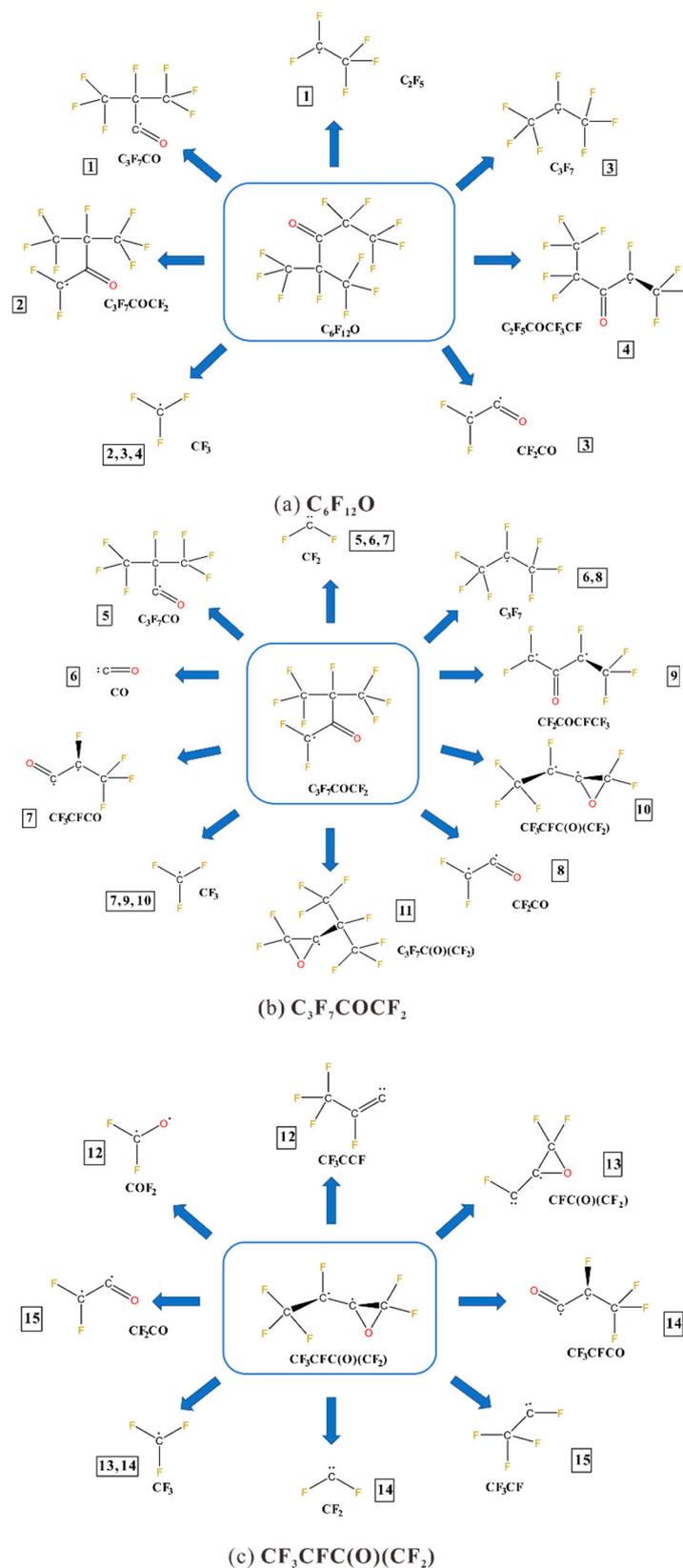


Figure 5. The proposed decomposition mechanisms of $C_6F_{12}O/CO_2$ [52].

In the presence of trace water, the produced HO and H aggravate the decomposition of $C_5F_{10}O$ and produce more new products, such as C_3F_7COH , C_3F_7OH , HF, and CF_2O . The ionization parameters of

the new formed products are lower than that of $C_5F_{10}O$, thus resulting in decreased dielectric strength. Furthermore, the newly formed CF_2O has an irritative effect on the skin and respiratory mucosa. HF can cause aggressive corrosion to equipment and irritation to humans [53]. Therefore, the presence of water negatively impacts the insulation performance of $C_5F_{10}O$.

During practical application, the insulating gas and equipment must have good compatibility to maintain security. Zhang et al. [54] systematically studied the compatibility between $C_6F_{12}O$ and metal materials by combining experimental tests and theoretical calculation. $C_6F_{12}O$ can be absorbed on the surface of Cu and Al due to chemical adsorption between $C=O$ and $C_6F_{12}O$, generating metal oxide. The interaction between $C_6F_{12}O$ and Ag is attributed to physical adsorption, and thus less $C_6F_{12}O$ was absorbed. Overall, from their SEM images, it was seen that $C_6F_{12}O$ did not cause serious corrosion to the surface of Cu, Al, or Ag even after reaction for 125 days. Thus, the compatibilities between $C_6F_{12}O$ and Cu, Al, and Ag were excellent.

5. Fluoronitrile (C_4F_7N)

Heptafluoro-iso-butyronitrile (C_4F_7N), one kind of fluoronitrile, was firstly prepared and commercialized by the 3MTM Company. It has the features of low toxicity and high thermal conduction. Its lifetime in the atmosphere is 22 years. The GWP is 2100, and its insulation strength is about one-fold higher than that of SF_6 under normal pressure. Its insulation property makes it a promising alternative to SF_6 in electrical insulation systems.

However, C_4F_7N cannot be applied alone due to its relatively high boiling point of $-4.7\text{ }^\circ\text{C}$. Thus, it is necessary to add other buffer gases to decrease the boiling point of insulating gas mixtures in practical applications. The breakdown voltage of C_4F_7N (12%)/ N_2 at 0.4 MPa was comparable to pure SF_6 at 0.2 MPa. Increasing the ratio of C_4F_7N in gas mixtures can effectively enhance the insulation strength. Considering the minimum temperature of $-25\text{ }^\circ\text{C}$ in practical application, the breakdown voltages of C_4F_7N (5%)/ N_2 at 0.3, 0.4, 0.5, and 0.6 MPa were 63.4%, 54.6%, 49%, and 56.4% of that of pure SF_6 , respectively. Moreover, the negative partial discharge inception voltages reached 80.4%, 66.9%, 62.8%, and 68.8% of that of pure SF_6 , respectively. The insulation strength of C_4F_7N/N_2 in a uniform electric field was higher than that in a non-uniform electric field [55]. The insulation strength and breakdown voltage of C_4F_7N (5%)/ N_2 were 83.34% of that of pure SF_6 . The breakdown voltage was maintained at 33.6 kV after 30 breakdown tests, indicating an excellent self-recovery property. The GWP of C_4F_7N (5%)/ N_2 was less than 600, which was far less than that of SF_6 (22,800). The probable decomposition pathways are shown in Figure 6. C_4F_7N mainly decomposed to four free radicals (CF_3 , CN , F , and C_3F_7) and the path from C_4F_7N to C_3F_4N and CF_3 was the most energy favorable. The free radicals react with each other form different products. CF_3 can react with CN , F , and other free radicals to generate products. Among the products, C_2F_6 , CF_4 , and CF_3CN are dominant. Although the products (e.g., CF_3CN and C_2F_5CN) were toxic, their concentrations were extremely low. Overall, the toxicity of the products was lower than that of the products of SF_6 decomposition, and was acceptable. Besides, N_2 was more likely to decompose than C_4F_7N . Thus, it acted as buffer gas and avoided the excessive decomposition of C_4F_7N , which ensured the insulation performance [56]. For C_4F_7N , the decomposed products were mainly C_3F_7 , CN , CNF , CF_3 , CF_2 , CF , CF_3CFCN (C_3NF_4), F , other free radicals, and CF_4 . Their amounts increased with the increase of temperature. The free radicals recombined with each other and generated products such as CF_4 , C_2F_6 , C_3F_8 , CF_3CN , CO , and so on. However, less C_4F_7N decomposed and less products were generated in C_4F_7N/CO_2 mixture due to the buffer action of CO_2 . At 2400 K, the amount of products in pure C_4F_7N was 96%, while that in C_4F_7N/CO_2 was 58%. Besides, the amount of CF_4 and C decreased after introducing CO_2 , thus avoiding the formation of precipitate carbon and other products with relatively inferior insulation performance [57,58].

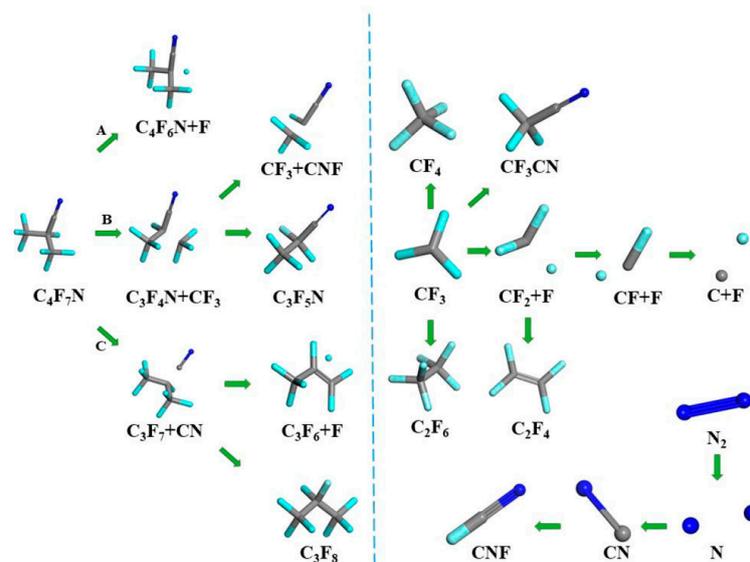


Figure 6. Probable decomposition pathways of C_4F_7N/N_2 [56].

The $H\cdot$ and $HO\cdot$ radicals generated from H_2O decomposition are active in reacting with free radicals decomposed from C_4F_7N during discharge (Figure 7). The activation energy in all possible paths with H_2O is lower than that without H_2O . Thus, the decomposition of C_4F_7N was accelerated, and the insulation performance was weakened. With the catalysis of H , the reactions generating HF , HCN , CF_3H , and other small molecules were more likely to occur. In the presence of $HO\cdot$, the reaction generating CF_3OH occurred easily. The products, including CF_2O , HF , HCN , CF_3CH_2CN , CF_2HCN , and CH_2FCN , are toxic, which would cause damage to operation personnel. HF and HCN would also cause severe corrosion to the equipment [59].

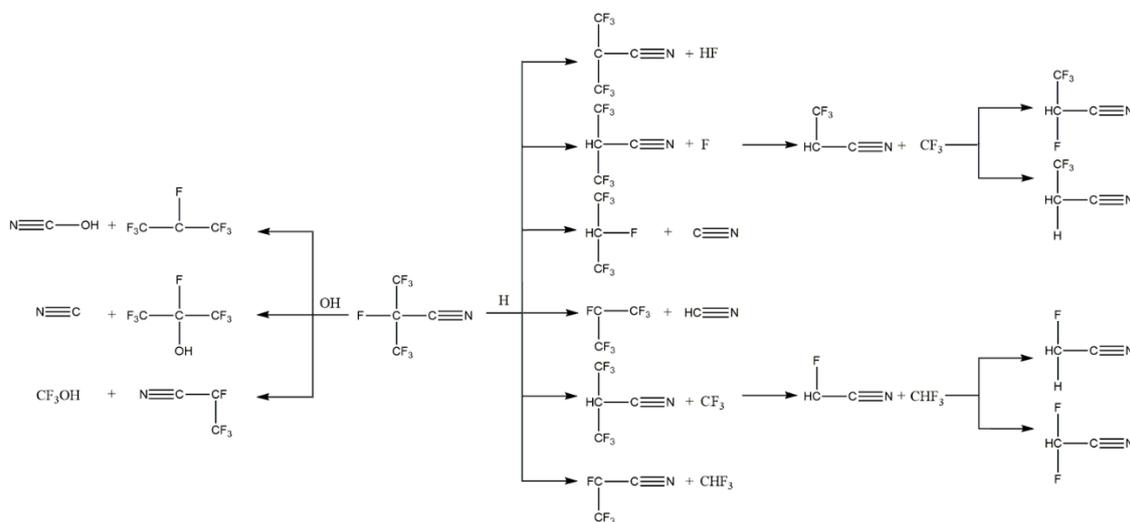


Figure 7. Decomposition pathways of C_4F_7N in the presence of H_2O .

Zhang et al. [60] studied the compatibility of C_4F_7N with Cu (1 1 1) and Al (1 1 1). They found that the interaction between C_4F_7N and Cu (1 1 1) or Al (1 1 1) was weak. The N atom was more likely than the F atom to react with Cu (1 1 1) or Al (1 1 1) and form a weak chemical bond. So, the compatibility of C_4F_7N with Cu (1 1 1) or Al (1 1 1) was good. They also studied the compatibility of decomposition products of C_4F_7N with Cu (1 1 1) and Ag (1 1 1). C_2F_5CN , CF_3CN , COF_2 , and CF_4 could be adsorbed on Cu (1 1 1) and Ag (1 1 1) surfaces by van der Waals force. The adsorption energies of products

on Ag (1 1 1) surface were weaker than those on Cu (1 1 1) surface. Overall, the compatibility of decomposition products of C₄F₇N with Cu and Ag were excellent [61].

6. Challenges and Perspectives

Most of the related studies were conducted based on theoretical calculation (e.g., DFT), and few experimental studies have been done to investigate the insulation performance in practical application—especially with the existence of trace H₂O or O₂, which is more close to reality. A certain amount of H₂O or O₂ may lead to the severe deterioration of insulation performance.

The compatibilities between the insulating gases or their decomposed products and metals were simulated and studied based only on a certain crystal face of metals. In electrical equipment, every crystal face can be exposed to the insulating gas. Thus, the actual compatibility between the insulating gases or their decomposed products and the insulation equipment may be very complex. It is significant to consider the compatibility through systematic experiments.

Common adsorbents such as γ -Al₂O₃ can not only absorb the hazardous products, but also the insulating gas. It would be interesting to design a novel adsorbent which could absorb the harmful products exclusively. This could ensure the safety of employees and equipment and maintain the insulation performance.

7. Conclusions

The GWPs of C₂F₆, C₃F₈, and *c*-C₄F₈ are still too high to show significant advantages compared with SF₆. CF₃I shows distinguished low GWPs and dielectric strength, however, it has been identified as a cancerogenic substance, and its stability and compatibility with the materials of electric equipment should be further studied. The GWPs of perfluorinated ketones (C₅F₁₀O and C₆F₁₂O) and fluoronitrile (C₄F₇N) are low, and they show high dielectric strengths and low toxicity, and therefore they have the potential to partially replace SF₆ in some electric insulation equipment. However, the compatibility of these insulating gases with the equipment materials, and the leaking rate obtained by using the conventional sealing materials should also be well studied. The adsorbents used to eliminate H₂O and O₂, which can accelerate the decomposition of the insulating gas, should also be screened or developed to ensure the safe operation of the equipment.

Author Contributions: Conceptualization, J.L.; investigation, L.Z. and Y.Z.; writing-original draft preparation, Y.W.; writing-review and editing, J.L.; project administration, D.H.

Funding: This research was funded by the project ‘Study on Physical, Chemical and Insulation Properties, and Engineering Demonstration of Environmental Insulating gas (I)-Project 3-Applied Feasibility Study of New Insulating Gas in Guangzhou Power Grid’, numbered as GZJKJXM20170330.

Conflicts of Interest: The authors declare no conflict of interest.

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