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Synthesis and dielectric properties of the eco-friendly insulating gas thiazyl trifluoride†

Jiayan Deng, [a] Min Peng, [a] Zhanyang Gao, [a] Yi Wang, [a] Baoshan Wang,[a] Wenjun Zhou,[b] Ruichao Peng *[a] and Yunbai Luo *[a]

Sulfur hexafluoride (SF_6), which is known as a superior electrically insulating and arc-quenching medium, plays a decisive role in the modern transmission and distribution network of electric energy, especially in high-voltage power networks. However, the ever-increasing usage of SF_6 also leads to the continuous escalation of atmospheric SF_6 levels, which is considered to be the main cause of the greenhouse effect. To decrease this environmental impact, eco-friendly alternatives to SF_6 have been researched for decades. To date, no significant success has been made regarding replacement gases for transmission networks. Some potential alternatives have comparatively lower global warming potential (GWP) but involve technical trade-offs. Thiazyl trifluoride, which has some excellent chemical and electric properties, is a novel substitution candidate for SF_6. In this article, an efficient synthetic route starting from sulfur monochloride and followed by ammonization and fluorination was proposed. The structures of the intermediates and the target products were determined by X-ray diffraction (XRD), infrared spectroscopy (IR), and gas chromatography-mass spectrometry (GC-MS). The effects of some determining factors on the yield and purity, including the molar ratio of the reactants, recrystallization conditions and condensation temperature, were also investigated. The results showed that the overall yield of thiazyl trifluoride was approximately 25%, while the purity could be up to 90.6% under optimal conditions.

Introduction

SF_6 is instrumental in achieving space-saving electrical energy transmission and distribution equipment, such as gas-insulated switchgears (GISs) and gas-insulated lines (GILs), due to its remarkable dielectric insulation and arc-quenching performance.[1,2] According to the report of The Intergovernmental Panel on Climate Change (IPCC) in 2013, the global warming potential (GWP) of SF_6 is approximately 23 000 times higher than that of CO_2, and SF_6 has a cumulative effect on global warming owing to its extreme chemical stability.[3] The Kyoto protocol has identified SF_6 as one of the six emission-limiting gases. Therefore, there is an urgent need to find a new environmentally friendly gas to replace SF_6.[4]

In recent years, researchers have been committed to finding environmentally friendly alternatives to replace SF_6; these alternatives should have low GWP, high dielectric strength and low

boiling point.[5,6] Significant efforts have been made to study insulation gases, and many researchers have made great progress using substitutes such as perfluorocarbons (*e.g.* c-C_4F_8, C_3F_8 (ref. 7)), hydrofluorocarbons, CF_3I,[8] $C_5F_{10}O$,[9,10] $C_6F_{12}O$ and C_4F_7N.[11,12] These alternatives have higher insulation strength and lower GWP than SF_6, but they also have different shortcomings in terms of boiling point, toxicity, stability, and other aspects. For example, although the insulation strength of c-C_4F_8 is approximately 1.25 times higher than that of SF_6 and the GWP is far below that of SF_6, the liquidus temperature of c-C_4F_8 is high (−8 °C), and carbon deposition will occur after discharge, which will affect equipment safety and insulation strength.[13,14] Similarly, C_4F_7N has to be mixed with CO_2 due to its high boiling point, which limits its insulation and arc-extinguishing performance.[15]

Thiazyl trifluoride (NSF_3) is commonly known as a chemically stable, colorless gas that is used as an important precursor for the preparation of various sulfur–nitrogen–fluorine compounds. Recently, the results of a quantum chemical calculation based on a structure-activity relationship model show that NSF_3 is most likely to be an insulating gas with a low greenhouse effect. Baoshan Wang *et al.*[16] suggested that NSF_3 has excellent performance parameters: the insulation strength is 1.35 times that of SF_6 at the same pressure, and the GWP value is 916, which is approximately one-twentieth that of SF_6, while the boiling point is −27 °C. Therefore, NSF_3 has been

[a]Engineering Research Center of Organosilicon Compounds & Materials, Ministry of Education, College of Chemistry & Molecular Sciences, Wuhan University, Wuhan 430072, P. R. China. E-mail: prc@whu.edu.cn; ybai@whu.edu.cn; Fax: +86-27-6875-2511; Tel: +86-27-6875-2511

[b]School of Electrical Engineering and Automation, Wuhan University, Wuhan 430072, P. R. China

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Fig. 3 Configuration of the high-voltage analysis platform.

The insulation performance of thiazyl trifluoride

A high-voltage analysis platform was applied to evaluate the insulation performance of NSF_3.[21] The configuration of the circuit is shown in Fig. 3, and the parameters are shown in Table 1. The measurement accuracy was within ±1%.

Two tungsten–copper alloy electrodes with diameters of 10 mm were employed as the test electrodes and positioned with a 2.5 mm-long interelectrode gap. The cavity was composed of a stainless-steel base, a sealed quartz-glass body, a charging/extracting valve and an electrode spacing adjustment screw. The unit can withstand a maximum pressure of 0.7 MPa.

The gas chamber was evacuated to vacuum and then filled with inert buffer gas after stabilization for 20 min. The procedure above was repeated three times to eliminate the effects of other impurities in the test chamber. The experimental gas was injected into the chamber until the pressure was equal to the saturated vapor pressure (absolute pressure at 20 °C). An increasing voltage method was applied to the discharge chamber through a power frequency voltage to determine the instantaneous breakdown voltage. The tests were conducted at least 5 times with a gap of 4 min between every two breakdowns.

The breakdown voltages of NSF_3 and SF_6 under the same conditions are shown in Table 2, which shows that the insulation strength of NSF_3 (whose purity was approximately 87%) was 1.28 times that of SF_6.

Results and discussion

Effects of the molar ratio of reactants on the yield of tetrasulfur tetranitride

According to previous studies, the yield was greatest when ammonia was passed through at a rate of 900–1000 mL min^{-1}.[22] However, the effect of ammonia on the reaction was related to not only its injection speed but also its total amount by affecting

Table 2 The dielectric strength of NSF_3 and SF_6

Gas	Pressure[a]/MPa	Purity[b]/%	Breakdown voltage/kV
SF_6	0.3	100	35.23
NSF_3	0.3	87	45.08

[a] Isolated pressure. [b] The impurities of NSF_3 were SF_6, CCl_3F, and SO_2, as determined by GC-MS.

the concentration of the reactants. Therefore, the reaction of ammonia to sulfur monochloride in a molar ratio from 6 : 1 to 17 : 1 was studied, and the synthetic route and results are displayed in Table 3. The yield of **2** increased from 30.3% to 73.8% as the molar ratio increased and then remained constant when the amount of ammonia reached over 16 equivalents of sulfur monochloride. Thus, the optimal molar ratio of sulfur monochloride to ammonia should be 1 : 16.

Effects of recrystallization conditions on the yield of tetrasulfur tetranitride

Sulfur was found to be the main impurity after removal of ammonium chloride by distilled water. Recrystallization was one of the most important steps in the preparation of S_4N_4. In addition to temperature, d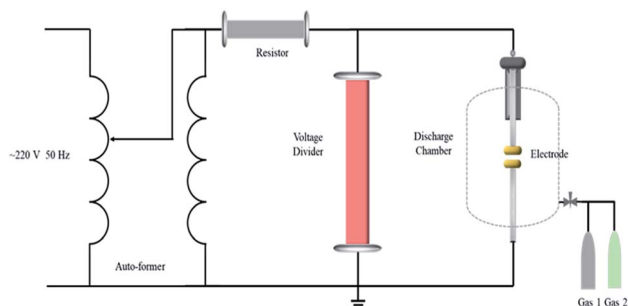iverse types of solvent could also directly affect the process of crystallization since the solubility varies by material. Nevertheless, the solubilities of S_4N_4 and sulfur were extremely similar; thus, choosing an appropriate

Table 3 Effects of the various molar ratios of sulfur monochloride to ammonia on the yield of **2**[a]

$$S_2Cl_2 \xrightarrow[CCl_4/-4°C/1\ h]{NH_3} S_4N_4$$
$$\quad 1 \qquad\qquad\qquad\qquad 2$$

Entry	S_2Cl_2 : NH_3	Yield[b] (%)
1	1 : 6	30.3
2	1 : 8	45.6
3	1 : 10	58.9
4	1 : 12	73.2
5	1 : 14	81.8
6	1 : 16	83.0
7	1 : 17	83.8
8	1 : 18	84.3

[a] Reaction conditions: S_2Cl_2 (0.19 mol), CCl_4 (100 mL), NH_3 at a rate of 1000 mL min^{-1}, at −4 °C for 1 hour. [b] Isolated yield.

Table 1 The parameters of the high-voltage test device

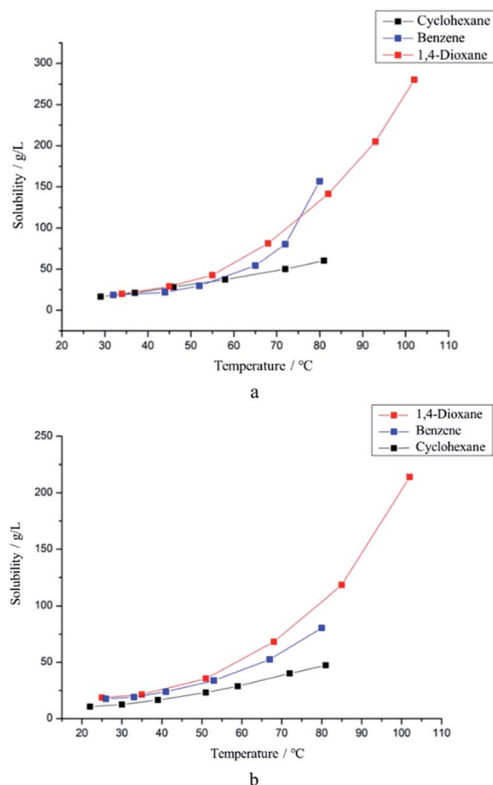| Rated voltage	Rated capacity	Max output voltage	Protective resistor	Voltage divider
220 V	10 kVA	100 kV	5 kΩ	1000 : 1

Fig. 4 (a) The solubility of S_4N_4 varies with temperature in three solvents. (b) The solubility of sulfur varies with temperature in three solvents.

solvent became key to improving the yield. Accordingly, benzene, 1,4-dioxane, and cyclohexane were selected as alternative solvents for recrystallization after taking polarity and boiling point into account; therefore, the dissolution differences in various temperature phases were tested. As shown in Fig. 4, the solubilities of S_4N_4 and sulfur in cyclohexane were relatively low, and the temperature sensitivities showed similar trends, which indicated that cyclohexane cannot be used as a solvent during the recrystallization process. By contrast, the solubilities of sulfur and S_4N_4 in 1,4-dioxane were higher than those of the other compounds. However, the solubility of sulfur was too sensitive to temperature, which resulted in the formation of a turbid liquid and eutectoid. Both S_4N_4 and sulfur can be well dissolved by benzene, which has a good thermosensitivity to S_4N_4. In general, benzene was treated as the optimal solvent for recrystallization.

Furthermore, the cooling temperature of crystallization was also a decisive factor; thus, reactions were carried out over a temperature gradient to verify the optimal temperature. Table 4 provides the relationship between recrystallization yield and cooling temperature. The results showed that the solution cooled rapidly, and the two substances were simultaneously precipitated by supersaturation at a low temperature (lower than 10 °C, entries 1–2). The yield of S_4N_4 increased obviously from 27.1% to 52.2% with the increase in temperature from 15 °C to 30 °C (entries 3–6). S_4N_4 precipitated first and separated from sulfur when the temperature ranged from 10–20 °C.

Table 4 Effect of cooling temperature on recrystallization yield[a]

Entry	Temperature/°C	Yield (%)
1	5	—[b]
2	10	—[b]
3	15	27.1
4	20	38.4
5	25	50.4
6	30	52.2
7	35	48.1

[a] Reaction conditions: impurity-containing S_4N_4 was dissolved by stirring with benzene, and the saturated solution was heated to 80 °C before cooling. [b] No expected product was obtained.

However, sulfur crystallized after some time, resulting in a low yield. As shown in Table 4, the optimum cooling temperature was 30 °C, and several orange needle-shaped crystals of good crystal shape were obtained at this time, while the yield was up to 52.2%. At this point, the cooling rate was moderate, which contributed to the formation of the S_4N_4 crystal nucleus, thus making it easier to avoid the precipitation of sulfur. Further heating accelerated the dissolution of S_4N_4, leading to a decrease in yield (entry 7).

Such efforts were made to promote the industrialization of the route. For instance, unpurified S_4N_4 was reacted with AgF_2, which resulted in a substantial amount of NSF_3 and effectively avoided environmental pollution by carcinogenic benzene. However, the purification process of gases remains to be further explored.

Effects of fluidizer on the yield of thiazyl trifluoride

This reaction was a combination of a S–N compound with a double-wedge cage structure and an active fluoride ion provided by silver difluoride. The reaction procedure is shown in Fig. 5. Apparently, the reactivity and mass of the active fluoride ion played key roles in the yield of NSF_3. We had already tried different kinds of fluorinating agents, such as KF (with 18-crown-6 as the phase transfer catalyst), CsF and AgF_2. The target product NSF_3 could only be obtained by AgF_2. It was worth noting that AgF_2 was highly susceptible to deterioration during
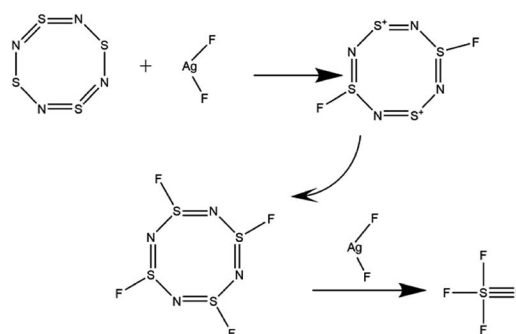

Fig. 5 Pathway for the synthesis of thiazyl trifluoride from tetrasulfur tetranitride.

the loading process, which would apparently result in the loss of a considerable amount of raw material, resulting in a low yield. Therefore, we investigated the effects of AgF_2 on the yield. As shown in Table 5, the yield of NSF_3 was found to increase from 21.32% to 57.38% (entries 1–5) when the $AgF_2 : S_4N_4$ molar ratio increased from 8 : 1 to 16 : 1, owing to the increase in the concentration of F^-. After that, the yield of NSF_3 approached a steady state at approximately 58% upon further addition of AgF_2 (entry 6). Based on our findings, it could be concluded that the optimal molar ratio of AgF_2 to S_4N_4 was 16 : 1, considering economic factors and reaction efficiency.

Effects of reaction conditions on the preparation of thiazyl trifluoride

NSF_3 was synthesized from S_4N_4 and AgF_2 by ring-opening fluorination; the three S–F single bonds were formed in a step-wise manner, which meant insufficient reaction time would result in a low crude yield of the product. Consequently, it was necessary to keep the reaction stable at a constant temperature for a period of time. William H. Kirchhoff reported that the whole process was approximately 3 hours. However, it was found that the yield increased from 28.12% to 57.15% as the reaction time was extended to 2 hours (as shown in Table 6). Further extension of the reaction time had no significant effect on yield; thus, the time should be controlled for approximately 2 hours to obtain the highest yield and maximum economic benefit.

To purify the target gas, GC-MS was used to identify the impurities in the crude product, and SF_6, CCl_3F and SO_2 were confirmed to be the main impurities. The multistage condensation method was used for further purification, in conjunction with a potassium permanganate solution and anhydrous calcium chloride. In consideration of the boiling point of NSF_3 and other impurity gases, ice-salt baths with different temperature gradients for condensation were set up, and the impacts on the purity are displayed below. By comparing the results shown in Table 7, it was found that the purity increased first and then decreased as the temperature decreased. Moreover, the purity of NSF_3 reached 90% when the condensing temperature was −15 °C. It was speculated that this result was because impurities whose boiling points were higher than that of NSF_3 were easier to liquefy and separate during the temperature reduction process. However, the target gas was also liquefied, and the gas flow rate decreased as the condensing temperature

gradually approached the boiling point of NSF_3, owing to the absence of an inert carrier gas, thereby leading to a decrease in the overall purity of the product. Therefore, it was suggested that the first-stage condensation temperature should be −15 °C to maximize the purity of NSF_3.

Hence, NSF_3 was successfully synthesized *via* a two-step reaction using sulfur monochloride, ammonia and silver(II) fluoride as raw materials. The total yield of NSF_3 was 25% under the optimal conditions, and the purity was over 90%.

Assessment of the thermal stability of thiazyl trifluoride

To evaluate the thermal stability of thiazyl trifluoride, normal vibration mode analysis was performed, and the vibration free energy at 298 K was estimated to predict the reaction free energy of the radical decomposition. The simulation of the gas phase radical decomposition reaction was performed with Gaussian

Table 6 Effects of reaction time on the yield of $NSF_3{}^a$

Entry	Time^b/h	Yield^c/(%)
1	0.5	28.12
2	1	35.35
3	1.5	43.03
4	2	57.15
5	2.5	57.54
6	3	57.68

^{a} Reaction conditions: S_4N_4 (3 mmol), AgF_2 (48 mmol), and CCl_4 (waterless, 30 mL). The reaction was carried out under stirring at 78 °C. ^{b} Timing began after AgF_2 was added. ^{c} Isolated yield, measured by GC-MS.

Table 7 Effects of condensing temperature on the purity of $NSF_3{}^a$

Entry	Condensing temperature/°C	Purity^b/%
1	−5	49
2	−10	60
3	−15	90
4	−20	82
5	−25	75

^{a} Reaction conditions: S_4N_4 (3 mmol), AgF_2 (48 mmol), and CCl_4 (waterless, 30 mL). The reaction was carried out under stirring at 78 °C for 2 hours, and the gas mixture was condensed at different temperatures. ^{b} GC purity.

Table 5 Effects of the $AgF_2 : S_4N_4$ molar ratio on the yield of $NSF_3{}^a$

Entry	Molar rate (AgF_2/S_4N_4)	Reaction time/h	Temperature/°C	Yield^b/(%)
1	8 : 1	2	78	21.32
2	10 : 1	2	78	32.32
3	12 : 1	2	78	44.79
4	14 : 1	2	78	53.44
5	16 : 1	2	78	57.38
6	18 : 1	2	78	58.27

^{a} Reaction conditions: S_4N_4 (3 mmol), CCl_4 (waterless, 30 mL), and AgF_2 were added in the specified proportions under stirring. ^{b} Isolated yield.

09 software. The geometries of all molecules were optimized by B3LYP/6-31G(d,p). The convergence threshold for geometry optimization was tighter than the default value (opt = tight), and tight grid integration was applied to perform DFT simulation (int = ultrafine).

The schematic illustration of radical decomposition is shown in Fig. 6, and we consider two types of bond cleavage between N–S and S–F to assess all the decomposition patterns.

All the structures of molecules after geometry optimization are listed in Fig. 7. For the first step of radical decomposition, one of the F or N atoms is deleted, forming a single radical molecule, which results in the $NSF_2^{\bullet}$ and $SF_3^{\bullet}$ as shown in Fig. 7B and C.

The reaction free energy for the radical decomposition reaction of the NSF_3 molecule is shown in Table S2.† The bond cleavage between F and S produces the lowest reaction energy (58.22 kcal mol^{-1}) and decomposition into molecules B. The other pathway produces molecules C and nitrogen radical, resulting in a reaction energy higher than 58.22 kcal mol^{-1}. Thus, it is difficult to decompose (especially radical nitrogen atom). The decomposition from $SF_3^{\bullet}$ to $SF_2^{\bullet}$ (as shown in Fig. 7D) and F radical has the lowest reaction energy in this system. All the simulation results listed above suggest the formation of $SF_2^{\bullet}$ radical. Furthermore, it has been confirmed that the thermal

Fig. 6 Schematic illustration of the radical decomposition of a molecule.

Fig. 7 Geometry of molecules after optimization with B3LYP/ 631G(d,p). (A) Geometry of NSF_3 molecules. (B) Geometry of NSF_2 after the first step of decomposition (losing a fluorine atom). (C) Geometry of SF_3 after the first step of decomposition (losing a nitrogen atom). (D) Geometry of SF_2 resulting from the decomposition of SF_3.

unimolecular decomposition or isomerization of NSF_3 is negligible even at extremely high temperatures (e.g., ∼3000 K whenever partial discharge or arc occurs).[16]

Comparison with other insulating gases

A comparison of the physical and environmental properties of NSF_3 and other mainstream potential substitute gases is shown in Table S3.† Although c-C_4F_8 has desirable insulating properties, the GWP remains high at 8700. Besides, c-C_4F_8 discharges at high energy may precipitate carbon, which may affect the insulation capacity. $C_5F_{10}O$ and C_4F_7N have disadvantages of their high boiling point (26.5 °C and −4.7 °C, respectively), so they need to be mixed with buffer gases to avoid the obstacle of high boiling point to a certain extent. The gas CF_3I exhibits high dielectric strength, low boiling point and GWP. However, it has been proven that iodine precipitation can be produced with high voltage and severe discharge, which may lead to a decline of dielectric strength. It can be concluded from the comparison that the performance of NSF_3 in various aspects is relatively excellent and has certain application prospects.

Conclusions

In this paper, an efficient and convenient synthesis route of thiazyl trifluoride from sulfur monochloride was developed. It is worth noting that this compound has the potential to be a novel eco-friendly insulating gas to replace SF_6 in high-voltage transmission systems. Sulfur monochloride reacted with ammonia in an ice bath to obtain tetrasulfur tetranitride. Afterwards, tetrasulfur tetranitride was fluorinated by AgF_2 and treated with multistage condensation to produce thiazyl trifluoride. The conditions of the relevant reactions were also optimized to maximize the yield and purity. The overall yield of NSF_3 was approximately 25%, and the purity was up to 90.6%, which has not been mentioned in previous research. The dielectric strength of NSF_3 was confirmed to be 1.28 times that of SF_6 through electrical experiments, indicating that NSF_3 might be a potential alternative to SF_6.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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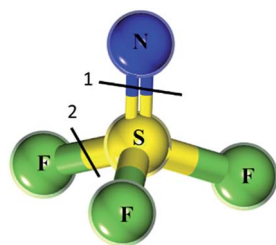
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