



# A simplified and efficient bromine-facilitated SF<sub>4</sub>-preparation method

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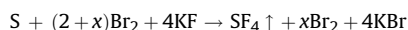
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## ABSTRACT

A novel, simple method for SF<sub>4</sub>-preparation has escaped discovery over the last 50 years of sulfur-fluorine chemistry and is described in the present study. Sulfur tetrafluoride is readily produced according to the equation:



The reaction is carried out either under autogeneous pressure at ambient or slightly raised temperature in a bomb tube, or in an open system at atmospheric pressure with mild heating and concomitant condensation of the product in a  $-78^\circ\text{C}$  cold-trap. Runs from the 5- to the 21-g-scale gave similarly good yields. The new SF<sub>4</sub>-producing method may be useful for laboratory preparation, and may also represent a new cost-effective alternative for industrial-scale production of this important fluorination reagent.

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## 1. Introduction

Sulfur tetrafluoride finds extensive use in inorganic and organic chemistry for the preparation of fluorides, effecting conversions of the type  $\text{COH} \rightarrow \text{CF}$ ,  $\text{C}=\text{O} \rightarrow \text{CF}_2$ ,  $\text{C}=\text{S} \rightarrow \text{CF}_2$ ,  $\text{COOH} \rightarrow \text{CF}_3$ ,  $\text{ROCOF} \rightarrow \text{ROCF}_3$  [1], and as a starting material for the synthesis of SF<sub>5</sub>Cl, SF<sub>5</sub>Br, S<sub>2</sub>F<sub>10</sub>, SF<sub>6</sub>, SOF<sub>4</sub>, SF<sub>5</sub>OCl and SF<sub>5</sub>OF, as well as for dialkylaminosulfurtrifluorides, which act much like SF<sub>4</sub> as fluorinating agents in organic chemistry [2]. The current worldwide annual consumption of SF<sub>4</sub> is thought to be several hundred metric-tons. Many reactions for the production of SF<sub>4</sub> have been investigated, but none is completely satisfactory, as corrosive chemicals, special equipment or dry solvents are required, and not every reaction is readily adapted to industrial scale-up, even if SF<sub>4</sub> is produced in good yield and purity. Unwanted by-products may also be formed. The reactions may be grouped in the following categories: F<sub>2</sub> + S or sulfur chlorides (with variations such as CoF<sub>3</sub> + S or ClF + SCl<sub>4</sub>) [3], Cl<sub>2</sub> + S + NaF (under pressure with heating up to 350 °C) [4], sulfur chlorides + NaF in a solvent (p-dioxane, acetonitrile) [4a], sulfur chloride + HF [5], sulfur or sulfur

chloride + Cl<sub>2</sub> + HF [6], IF<sub>5</sub> + S [4a,7], (HF)<sub>n</sub>-amine + S<sub>n</sub>Cl<sub>2</sub> + Cl<sub>2</sub> [8] and sulfur chlorides + NOF [9].

## 2. Results and discussion

### 2.1. Bromine-facilitated synthesis of SF<sub>4</sub>

A novel method has been discovered that can produce SF<sub>4</sub> in a state of high purity, in a short time period, with good to excellent chemical yield, and minimal set-up requirements; the starting materials are sulfur, bromine and potassium fluoride. The method is analogous to the reaction that utilizes NaF, sulfur and chlorine [4], but uses KF instead of NaF, and Br<sub>2</sub> instead of Cl<sub>2</sub>. Results using metal fluorides other than KF in our new SF<sub>4</sub>-producing reaction will be discussed later. The reactants are mixed in a steel bomb tube and either set aside for several days at ambient temperature, or heated at 70–86 °C for about 8 h. The product is recovered by vacuum-condensation from the reactor held at  $-78^\circ\text{C}$ . As an alternative to running the reaction under autogeneous pressure, the product may be collected in a  $-78^\circ\text{C}$  cold-trap using a system equilibrated with atmospheric pressure (open-atmosphere). In this latter case, the heated (60–70 °C) steel bomb tube is fitted with a cooled, upright steel pipe serving as a reflux column, the upper end of which is connected via a polytetrafluoroethylene or polyethylene tube to a  $-78^\circ\text{C}$  cold-trap. Variations of reaction conditions and yields are summarized in Table 1. In runs B and F, a higher proportion of bromine was used than in runs A, C and E, to ensure

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**Table 1**  
Syntheses of SF<sub>4</sub> from KF+S+bromine.

Run	Charge [g]	Ratio S:KF:Br <sub>2</sub>	Time [h, d] t [°C]	Yield [g]	Yield [%]
A Bomb tube	S: 4.69 KF: 34.7 Br <sub>2</sub> : 83	1.00:4.08:3.54	8 d/ambient	14.3	90, pure
B Bomb tube	S: 3.24 KF: 24.2 Br <sub>2</sub> : 86.4	1.00:4.10:5.30	6 d/ambient	11.5	96, pure
C Bomb tube	S: 2.3 KF: 17.1 Br <sub>2</sub> : 36.3	1.00:4.08:3.20	3 h/60 °C 2 h/72 °C 4 h/80–86 °C	6.7	86, pure
D Bomb tube	S: 1.53 KF: 11.75 Br <sub>2</sub> : 31.3	1.00:4.24:4.09	44 h/57 °C +6 d/ambient +6 d/ambient	4.06 4.87 5.09	79, pure 94.5, pure 98.6, pure
E Bomb tube	KF: 24.12 S: 3.16 Br <sub>2</sub> : 31.1	1.00:4.02:1.97	1 d/ambient, 18 h/80 °C	7.5	70, pure
F Metal distill	KF: 62.1 S: 8.61 Br <sub>2</sub> : ≈300 (90 ml)	1.00:3.98:≈7.0	10 h/60–70 °C	21	71, pure

Pure = decolorized with Hg; identification by infrared spectroscopy.

**Table 2**  
Weight% SF<sub>4</sub> yield (based upon S) correlations in Run D.

Weight of SF <sub>4</sub> (% yield SF <sub>4</sub> )	Weight of recovered Br <sub>2</sub> (% yield SF <sub>4</sub> ) <sup>a</sup>	Weight of salt residue KBr + KF (% yield SF <sub>4</sub> ) <sup>a</sup>	Consumed Br <sub>2</sub> , as weight AgBr (% yield SF <sub>4</sub> ) <sup>a</sup>
5.09 g (98.6%)	15.68 g (102%) <sup>a</sup>	23.25 g (98.6%) <sup>a</sup>	35.19 g (98.4%) <sup>a</sup>

<sup>a</sup> Implied % yield SF<sub>4</sub>, with sulfur as the limiting reagent.

that a liquid phase was always present. The KF is anhydrous and has a fine-grained consistency, and additionally, is dried in the reactor under high vacuum for 1–2 h. After cooling, sulfur and bromine are added, which is best accomplished by first adding the sulfur and then pouring the bromine in through a funnel. The reactor is then either immediately sealed, or connected to the stainless steel pipe acting as a reflux column. Slight warming of the bomb tube occurs upon adding the bromine. Since bromine reacts with sulfur very slowly and without evolution of heat at ambient temperature [10], the temperature increase may be due to the exothermic formation of a complex KF·Br<sub>2</sub> [11]. Heating is immediately commenced, and in the case of open-atmosphere production of SF<sub>4</sub>, formation of a liquid condensate in the –78 °C cold-trap is evident, after about 30 min (Run F). The increase in liquid level in the cold-trap slows down noticeably after 3–4 h, and after about 10 h resulted in a yield of 71% of SF<sub>4</sub> (Run F). This yield does not take into account the hold-up of the open system, which is estimated at 2 g of SF<sub>4</sub>. Because in the reaction of S + Br<sub>2</sub>, S<sub>2</sub>Br<sub>2</sub> [12] is initially formed, it is assumed that a reaction sequence occurs which is analogous to that in the reaction of KF with S<sub>2</sub>Cl<sub>2</sub> or SCl<sub>2</sub>, resulting in SF<sub>4</sub>.

Net reaction:



With excess bromine and KF:

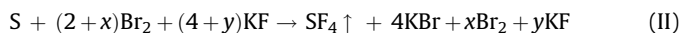
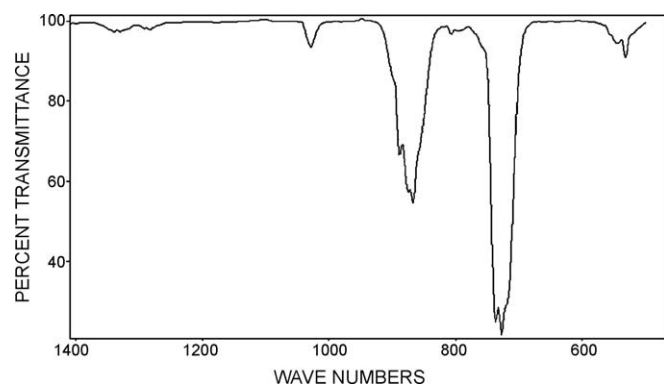


Table 2 summarizes the additional results of exhaustive Run D, which was used to correlate the amounts of reagents consumed with the weights of the products formed. The yield of 98.6% of SF<sub>4</sub> highly correlates with sulfur as the limiting reagent, and with the weight of the recovered bromine, the weight of the salt residue (consisting of excess and unconsumed KF and KBr formed), and the

weight of bromide (as determined by gravimetric analysis as silver bromide), confirming Eq. (II), above.

The deviation in recovered bromine is undoubtedly caused by the small losses occurring upon isolating the SF<sub>4</sub>, which invariably leads to the co-transfer of some bromine. This (small) loss of bromine implies a larger bromine consumption than could have possibly occurred according to Eq. (II), and leads to a small overestimation of the SF<sub>4</sub> yield (an implied SF<sub>4</sub> yield of 102%). The close agreement of all values obtained from weights confirms the net reaction as given in Eq. (I), above. All of the values in Table 2 represent a lower limit due to inevitable losses in transfers and the reaction may therefore go practically to an extent of 100% of theory. The infrared spectrum of the product [13] shows weak bands corresponding to SOF<sub>2</sub> and SiF<sub>4</sub> as the only trace impurities. A infrared spectrum of our SF<sub>4</sub> product from run “F” is shown in Fig. 1.



**Fig. 1.** Crude SF<sub>4</sub> gas was synthesized and isolated as described in the results using reflux-condensation (distillation) in stainless steel (Run F). SF<sub>4</sub> was transferred into a stainless steel sample cell (4 Torr) and analyzed using FITR, as described in Section 4.

The SF<sub>4</sub> was also made in an all-glass apparatus at atmospheric pressure, with immediate condensation of the SF<sub>4</sub> product, but notable increases in SOF<sub>2</sub> and SiF<sub>4</sub> contamination were observed in the IR spectrum. The extreme sensitivity of SF<sub>4</sub> to water requires extreme dryness of the glass apparatus, which is difficult to achieve.

## 2.2. General comments regarding bromine-facilitated synthesis of SF<sub>4</sub>

The reactions were run in ratios of S:KF:Br<sub>2</sub> = 1.0:≈4.1:≈(2–7) (Table 1).

No evidence was found in the infrared spectrum of the product for the presence of S=SF<sub>2</sub> or FSSF, which should be the primary products of reaction of S<sub>2</sub>Br<sub>2</sub> + KF, as they are in the reaction of S<sub>2</sub>Cl<sub>2</sub> + KF [14]. These molecules easily disproportionate (e.g. 2FSSF → 2S=SF<sub>2</sub> → (3/8)S<sub>8</sub> + SF<sub>4</sub>; or 2S=SF<sub>2</sub> → (1/4)S<sub>8</sub> + 2SF<sub>2</sub>; 2SF<sub>2</sub> → S<sub>2</sub>F<sub>4</sub> → (1/8)S<sub>8</sub> + SF<sub>4</sub>), and some of the steps are catalyzed by Lewis acids such as HF, which is likely present in these reactions [14]. The sulfur produced in the dismutation 2S<sub>2</sub>F<sub>2</sub> → SF<sub>4</sub> + (3/8)S reacts again with bromine and eventually all sulfur is thus converted into SF<sub>4</sub>, as evidenced by the nearly quantitative yield of SF<sub>4</sub> in several of the runs in Table 1. Although the sequence of chemical conversions must be complex, the net reaction is very simple (Eq. (1)). In the bomb tube test run “E” at ≈80 °C with the nearly exact stoichiometric amounts of reactants (S:KF:Br<sub>2</sub> = 1:4:2), 70% of SF<sub>4</sub> was obtained, while with an excess of bromine, but a shorter reaction time, the yield was 86% (Run C), and can be as high as nearly 99% (Run D) with a longer reaction time. Thus, the use of excess bromine appears to be very advantageous. All reactions listed in Table 1 have been run with sulfur as the limiting reagent. From a practical point of view, it might be preferable to have KF as the limiting reagent and utilize all of the KF (100%), since it is possible to completely remove excess sulfur bromide and bromine by distillation and re-use these reagents. In this case, the residue would consist only of KBr. However, running the reaction with a one-fold excess of sulfur resulted in a much lower yield of SF<sub>4</sub> (20% of theoretical), thus implying that the optimal reactant parameters appear to be close to the stoichiometric ratio of 1:4 for S and KF, respectively.

## 2.3. Use of metal fluorides other than KF

Replacing KF with NaF produces at most traces of SF<sub>4</sub>. Neither SF<sub>4</sub> nor SOF<sub>2</sub> (by infrared spectroscopy) are formed at lower temperatures (r.t.: 2 d; 80 °C: 18 h) from a mixture of 4NaF + S + 3Br<sub>2</sub> in a bomb tube. Only upon heating (155 °C: 18 h), traces of SOF<sub>2</sub> are detectable in the infrared spectrum, so that apparently minuscule amounts of SF<sub>4</sub> are produced under these comparatively extreme conditions, which hydrolyze with traces of adventitious water. This result can likely be attributed to less favorable energetic changes for the conversion of NaF → NaBr, as opposed to KF → KBr. Fluorides with a larger cation than that of K (e.g. RbF, CsF, NR<sub>4</sub>F) are also expected to produce SF<sub>4</sub>, but were not examined.

## 3. Conclusions

The new preparation method for SF<sub>4</sub> (S + (2 + x)Br<sub>2</sub> + 4KF → SF<sub>4</sub>↑ + xBr<sub>2</sub> + 4KBr) may represent a significant improvement over many previously-used methods of producing SF<sub>4</sub>, as the reaction requires only commonly-used, inexpensive and commercially-available reactants, and can be run in open reactor systems (at atmospheric pressure) at ambient to modestly-elevated temperatures, using standard laboratory equipment and instrumentation. The new bromine-facilitated reaction, under some conditions, can produce SF<sub>4</sub> yields of up to 99% of theoretical, and can also produce

good yields in as little as 5–10 h. The SF<sub>4</sub> product is easily separated from unused Br<sub>2</sub> and sulfur bromides by condensation, and final purification is accomplished by treatment with Hg (or other metals, or sulfur). The unreacted Br<sub>2</sub> and sulfur bromides may be easily removed from the solid residue (excess metal fluoride, metal bromide) and can be reutilized in the subsequent production runs of SF<sub>4</sub>. Potassium bromide is produced in this reaction as well, and might be considered a useful by-product for bromine or KBr manufacture. In summary, the new bromine-facilitated method of producing SF<sub>4</sub> from metal fluoride and sulfur may represent a promising low-cost synthetic route to this important fluorination reagent.

## 4. Experimental

### 4.1. Materials

Anhydrous fine-grain potassium fluoride powder is from Aldrich Chemical Company, Milwaukee, USA (99%). Flowers of sulfur (technical grade) and bromine (ACS grade) were purchased from Nurnberg Scientific in Portland, Oregon, USA, and both were used as received.

### 4.2. Infrared cell and analysis

Infrared (IR) spectral analysis of the gas-phase reaction products were performed using a Fourier transform infrared spectroscopy (FTIR) Galaxy 4020 (Mattson Instrument, Inc.) spectrometer. IR spectra were analyzed with Mattson Enhanced First and WinFirst Software. After initial use of a cell made of glass, it was found that using a metal cell (stainless steel, l = 5 cm, KBr-windows) was very advantageous. A sample of SF<sub>4</sub> in the glass cell at p 2–10 Torr was converted within 1–1.5 h into SOF<sub>2</sub>, highlighting the moisture sensitivity of SF<sub>4</sub>. After using the metal cell, the apparent contamination signal (SOF<sub>2</sub>) in the SF<sub>4</sub>-sample was always much diminished and often practically absent and constant over time. The metal cell was passivated by keeping it under an SF<sub>4</sub>-pressure of about 200 Torr for 2 h, followed by evacuation (high vacuum) for several hours.

### 4.3. General remarks

Because of hazards associated with the use of bromine and production of SF<sub>4</sub>, all relevant procedures were performed within a well-ventilated chemical fume hood, using good laboratory practices. Runs B, C, D and F are described in detail. A, C and E were run in a like manner. All details are listed in Table 1. Bromine may be added either by vacuum-condensation or manually pouring into the open reaction vessel. When the reaction was run in a sealed bomb tube that was not evacuated immediately after all reactants had been combined, the valve was opened slowly at the isolation step (reactor at –78 °C) in order to pump out the air slowly and thereby avoid unnecessary loss of product; alternatively, the reactor could be evacuated at –196 °C immediately after sealing.

#### 4.3.1. Synthesis of SF<sub>4</sub> at ambient temperature and under autogeneous pressure (Run B)

Potassium fluoride (24.2 g) was dried in a 300-ml stainless steel Hoke bomb tube under high vacuum at 150–200 °C for about one hour. After cooling, flowers of sulfur (3.24 g) were added and after re-sealing, bromine (86.4 g) was added by vacuum-condensation, giving a molar ratio of S:KF:Br<sub>2</sub> = 1.00:4.10:5.30. After keeping the reactor for 3 days at room temperature, a strong SF<sub>4</sub>-signal was evident in the infrared spectrum of a gas sample, and after another 3 days at room temperature, the SF<sub>4</sub>-signal appeared considerably

more intense. The reactor was cooled to  $-78\text{ }^{\circ}\text{C}$  (dry-ice acetone bath) and connected through a liquid-nitrogen trap to a vacuum pump. After pumping for 1.5 h, when the transfer had come virtually to an end, a light brown condensate was obtained. This was decolorized by treatment with  $\approx 10\text{ g}$  of Hg in a Carius tube ( $V = 1.5\text{ l}$ ) at ice-temperature. The product was condensed into a trap ( $-196\text{ }^{\circ}\text{C}$ ), and upon melting produced a colorless liquid with a low boiling point. The infrared spectrum (2 Torr) was that of  $\text{SF}_4$  with a small contaminant-band of  $\text{SOF}_2$ .

#### 4.3.2. Synthesis of $\text{SF}_4$ at moderately-elevated temperature (Run C)

As in the previous example, KF (17.1 g) was dried in a 300-ml bomb tube. After cooling, sulfur (2.3 g) was added, followed by bromine (36.3 g) poured from a measuring cylinder. Upon adding the bromine a slight warming of the reactor was noted. The vessel was immediately sealed and heated at  $60\text{ }^{\circ}\text{C}$  for 3 h, then cooled to  $-78\text{ }^{\circ}\text{C}$  and the volatile contents pumped into a  $-196\text{ }^{\circ}\text{C}$  trap until no more transfer had occurred, as assessed by visual inspection of the cold-trap at the liquid-nitrogen level. The weight of the product indicated that a chemical yield of 50% had been attained at this point. After re-condensing the product into the reactor at  $-196\text{ }^{\circ}\text{C}$ , heating was continued for 2 h at  $72\text{ }^{\circ}\text{C}$ , and then 4 h at  $82\text{--}86\text{ }^{\circ}\text{C}$ . The product was isolated and decolorized as in the previous example. The resultant yield was equal to 6.7 g, or 86% of theory. The infrared spectrum was that of  $\text{SF}_4$  contaminated with small amounts of  $\text{SOF}_2$ .

#### 4.3.3. Synthesis of $\text{SF}_4$ with extended time of reaction (Run D)

The quantities of the reagents and reaction conditions are given in Table 1. The product was isolated as in Section 4.3.2 above, after the reaction times given in Table 1, respectively, then weighed after debromination, and finally collected in a tared steel storage vessel. The weights represent those of pure product collected at each time point. Pumping was in every case continued until transfer into the cold-trap had practically ceased, as judged from visual inspection of condensation as described in Section 4.3.2 above. At the end of the product transfer, excess bromine was pumped exhaustively into a separate cold-trap ( $-196\text{ }^{\circ}\text{C}$ ), while the reaction bomb tube was heated in a boiling water bath. The mass of the salt residue was determined by weighing the bomb tube before and after washing with  $\approx 130\text{ ml}$  of water (the wash solution). Silver bromide was precipitated by adding a slight excess of  $\approx 30\%$  aqueous  $\text{AgNO}_3$ -solution to the acidified (5 drops of conc.  $\text{HNO}_3$ ) wash solution, filtered, washed thoroughly with water, sucked dry overnight and finally, further dried under vacuum.

#### 4.3.4. Synthesis of $\text{SF}_4$ at atmospheric pressure (Run F)

KF (62.1 g) was dried in a 300-ml steel bomb tube as described above, and after cooling, sulfur (8.61 g) and bromine (90 ml,  $\approx 300\text{ g}$ ) were added. The reactor was attached at once to a steel tube (500 mm  $\times$  6.2 mm with threads fitting into the bomb tube threads) acting as a reflux column and connected via a Teflon tube to a large cold-trap, held at  $-78\text{ }^{\circ}\text{C}$ . This cold-trap was connected to a second smaller cold-trap, also held at  $-78\text{ }^{\circ}\text{C}$ , which allowed pressure equilibration to the atmosphere, condensing out any atmospheric moisture and thereby guaranteeing absolute dryness in the sample-collecting cold-trap. The bomb tube was heated for 10 h in a water bath at  $60\text{--}70\text{ }^{\circ}\text{C}$ . Condensation of product in the first cold-trap was evident after 30 min. After 4–5 h, further increase in the liquid-product level in the first cold-trap was difficult to assess. The weight of crude product after 10 h corresponded to  $\approx 80\text{--}85\%$ . In order to separate the  $\text{SF}_4$  product from colored contaminants (bromine, possibly sulfur bromides), the product was twice vacuum-transferred from the container at  $-78\text{ }^{\circ}\text{C}$  into a cold-trap at  $-196\text{ }^{\circ}\text{C}$ . This resulted in 21 g of a nearly colorless product, with a corresponding infrared spectrum indicating  $\text{SF}_4$  and only trace amounts of  $\text{SOF}_2$  and  $\text{SiF}_4$  (see Fig. 1).

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