(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
17 December 2009 (17.12.2009)

PCT

(10) International Publication Number
WO 2009/152385 A2

(51) International Patent Classification:
C01B 17/45 (2006.01) *C01B 9/08* (2006.01)

(21) International Application Number:
PCT/US2009/047116

(22) International Filing Date:
11 June 2009 (11.06.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

61/060,642	11 June 2008 (11.06.2008)	US
61/153,180	17 February 2009 (17.02.2009)	US
61/176,674	8 May 2009 (08.05.2009)	US

(71) Applicant *(for all designated States except US)*: **AVANTBIO CORPORATION** [US/US]; 2515 Ne 104th Street, Vancouver, WA 98686 (US).

(72) Inventor; and

(75) Inventor/Applicant *(for US only)*: **WINTER, Rolf** [DE/US]; 3220 Se 56th Ave, Portland, OR 97206 (US).

(74) Agent: **WINGER, Rachal, C.**; K&l Gates LLP, 925 Fourth Avenue, Suite 2900, Seattle, WA 98104-1158 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

WO 2009/152385 A2

(54) Title: BROMINE-FACILITATED SYNTHESIS OF FLUORO-SULFUR COMPOUNDS

(57) Abstract: Described herein are methods for the bromine-facilitated synthesis of fluoro- sulfur compounds, that include SF_4, SF_5CI, SF_5Br and SF_6. The methods described herein generally require lower temperature and pressure, produce higher yields, require less time, do not use corrosive or costly reactants and solvents that are commonly used in the synthesis of the fluoro-sulfur compounds, and do not produce deleterious waste products when compared to previously-used methods.

BROMINE-FACILITATED SYNTHESIS OF FLUORO-SULFUR COMPOUNDS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application No. 61/060,642, filed June 11, 2008, U.S. Provisional Patent Application No. 61/153,180, filed February 17, 2009, and U.S. Provisional Patent Application No. 61/176,674, filed May 8, 2009, the entire disclosures of which are incorporated herein by reference.

FIELD OF THE INVENTION

[0002] Disclosed herein are methods of synthesizing fluoro-sulfur compounds. The disclosed methods use bromine to promote the synthesis of fluoro-sulfur compounds while avoiding the use excessive temperatures, electrochemical preparation, or the use of traditionally used solvents or reactants generally deemed less desirable due to toxicity, excess reactivity or cost.

BACKGROUND OF THE INVENTION

[0003] A number of fluoro-sulfur compounds have beneficial applications. For example, sulfur tetrafluoride (SF_4) is a widely-used compound produced yearly at the metric ton level, which can be utilized as a deoxofluorinating reagent in converting carboxylic acids, aldehydes, some alcohols and ketones into their corresponding deoxofluorine derivatives (*i.e.* R-CF_3, R-CHF_2, RF, RR'-CF_2). SF_4 is also utilized as an etching agent in the electronics industry. Moreover, SF_4 can be utilized as a precursor for the synthesis of other important fluorinated products such as, without limitation, pentafluorosulfur chloride (SF_5Cl), pentafluorosulfur bromide (SF_5Br), and sulfur hexafluoride (SF_6).

[0004] Sulfur hexafluoride (SF_6), is a compound that is produced by the thousands of metric tons each year, and its worldwide uses include: acting as a PCB replacement and an inert dielectric medium for electrical equipment, the etching of semiconductors, the casting of magnesium, the manufacture of thermal windows, a source of thrust in some rocket propulsion systems, the tracing of air flow through industrial systems, a tamponade for retinal holes of the eye and in medical imaging.

[0005] Compounds harboring fluoro-organic modifications such as R-CF_3, R-CHF_2, RF, RR'-CF_2 and RSF_5, have been used in a variety of applications including fluorinated therapeutic and diagnostic drugs, pesticides, herbicides, antibiotics, perfluorinated blood substitutes, fungicides, polymer solvents, polymers, lubricants, liquid crystals, surface-active agents, high-boiling solvents, stable solvents, electrically conducting polymers and the like. Utilizing an SF_5 group in the place of CF_3 offers many advantages. Particularly, the SF_5 group possesses greater electronegativity than CF_3. Moreover, compounds containing SF_5 may be further distinguished by their outstanding chemical properties including high to extreme chemical and thermal stability, hydro- and oleophobicity, lipophilicity, high-density, reduction of shock sensitivity in explosives, low boiling point, low polarizability and low surface tension.

[0006] While SF_5-derivatives offer these advantages, they have been difficult to synthesize. The difficulty of obtaining such compounds is in part related to the difficulty of obtaining sufficient and affordable quantities of SF_5Cl or SF_5Br, which are the principal chemical reagents used to synthesize and obtain a number of organic or inorganic derivatives that bear the SF_5-radical moiety. SF_5Cl, particularly, is a valuable reactant to produce SF_5-radical bearing derivatives of (sulfur hexafluoride) SF_6 and may be reduced to disulfur decafluoride (S_2F_{10}) with the latter being converted into pentafluorosulfur bromide (SF_5Br). SF_5Cl can also be used in the synthesis of SF_6. It is of interest that SF_5Cl can be particularly used in the manufacture of SF_6 by a pyrogenic route (*e.g.* US Patent No. 4,390,511), whereby a disproportionation occurs according to the following reaction:

$$SF_5Cl \rightarrow \tfrac{1}{2}\, SF_6 + \tfrac{1}{2}\, SF_4 + \tfrac{1}{2}\, Cl_2$$

In this method, SF_6 is obtained that is free of S_2F_{10}, a compound believed to be highly toxic and a by-product of the manufacture of SF_6 by the reaction of sulfur with fluorine. Accordingly, the use of SF_5Cl can be used to produce high purity SF_6.

[0007] Collectively, a variety of methods have been demonstrated as processes for the production of SF_6 and include US Patent Nos. 2,883,267, 2,912,307, 3,054,661, 3,345,277, 3,399,036, 3,373,000, 4,390,511, 5,639,435 and Japanese Patent No. 7,625,497. These methods frequently employ electrochemical preparation, high

reaction temperatures and pressures, and/or utilize highly-reactive and/or costly reactants that can include F_2, SF_5Cl, IF_5, SF_4, ClF and HF.

[0008] SF_5Br is also a valuable chemical compound that has been demonstrated as a reactant for the efficient production of SF_5-radical bearing chemicals; also known as derivatives of SF_6.

[0009] Currently available methods of producing fluoro-sulfur compounds suffer a number of drawbacks. The drawbacks generally include the use of excessive temperatures, electrochemical preparation, expensive and/or hazardous reactants, the requirement for numerous successive steps or long reaction times, the production of low or variable yields and/or the generation of toxic by-products. Accordingly, there is room for improvement in the synthesis of fluoro-sulfur compounds.

SUMMARY OF THE INVENTION

[0010] Described herein are methods for the synthesis of fluoro-sulfur compounds, more specifically SF_4, SF_5Cl, SF_5Br and SF_6. The methods described herein generally require lower temperatures and pressure, produce high yields, in some cases require less time, do not use highly reactive oxidants or costly reactants and solvents that are commonly used in the synthesis of fluoro-sulfur compounds, and do not produce deleterious waste products when compared to previously-used methods.

[0011] One embodiment disclosed herein includes a method of producing a fluoro-sulfur compound or a compound made using the produced fluoro-sulfur compound comprising: admixing Br_2, a metal fluoride reactant, and a sulfur reactant thereby initiating a reaction that produces a yield of the fluoro-sulfur compound of greater than about 10%. In another embodiment, the admixing further includes Cl_2. In another embodiment, the reaction proceeds at temperature of about 10 to about 400°C. In another embodiment, either S_2F_{10} or BrF, BrF_3, BrF_5, $CsBrF_4$, $CsBrF_2$, acetonitrile, Dioxane, ClF, ClF_3, NOF, HF, F_2, $(HF)_n$•amine, IF_5 or combinations thereof are not added to the reaction.

[0012] Embodiments disclosed herein also include methods of producing SF_4 or a compound made using the produced SF_4. In one embodiment the method includes

admixing a sulfur reactant, a metal fluoride reactant, and a Br_2 reactant thereby initiating a reaction that produces SF_4 at a yield of greater than about 10%. In another embodiment of producing SF_4 or a compound made using the produced SF_4, the reaction proceeds at a temperature of about 10 to about 400 °C.

[0013] In another embodiment of producing SF_4 or a compound made using the produced SF_4, the sulfur reactant is S and the metal fluoride is KF and the admixing occurs at a stoichiometric ratio of about 4KF to about $2Br_2$ to about 1 S and the reaction proceeds at a temperature of about 10 to about 400°C.

[0014] In another embodiment of producing SF_4 or a compound made using the produced SF_4, the metal fluoride is an alkaline earth metal fluoride, an alkali metal fluoride, CsF, RbF, KF, BaF_2, SrF_2 or a combination thereof and/or the sulfur reactant is S, S_2Cl_2, SCl_2, S_2Br_2, SBr_2 or a combination thereof.

[0015] In an additional embodiment of producing SF_4 or a compound made using the produced SF_4, the method includes admixing a sulfur reactant, a metal fluoride reactant, a Cl_2 reactant and a Br_2 reagent thereby initiating a reaction that produces SF_4 at a yield of greater than about 10%. In another embodiment of producing SF4 or a compound made using the produced SF_4, the reaction proceeds at a temperature of about 10 to about 400 °C.

[0016] In another embodiment of producing SF_4 or a compound made using the produced SF_4, the sulfur reactant is S and the metal fluoride is KF and the admixing occurs at a stoichiometric ratio of about 4KF to about 1 Br_2 to about 1 S to about $2Cl_2$ or the sulfur reactant is SCl_2 and the metal fluoride is KF and the admixing occurs at a stoichiometric ratio of about 4KF to about 1 Br_2 to about 1 SCl_2 to about 1 Cl_2 and the reaction proceeds at a temperature of about 10 to about 400 °C.

[0017] In another embodiment of producing SF4 or a compound made using the produced SF_4, the metal fluoride is an alkaline earth metal fluoride, an alkali metal fluoride, CsF, RbF, KF, BaF_2, NaF, SrF_2 or a combination thereof and/or the sulfur reactant is S, S_2Cl_2, SCl_2, S_2Br_2, SBr_2 or a combination thereof.

[0018] Embodiments disclosed herein also include methods of producing SF_5Cl or a compound made using the produced SF_5Cl. In one embodiment the method includes admixing a Cl_2 reactant, a sulfur reactant, a metal fluoride reactant, and Br_2 reagent thereby initiating a reaction that produces the SF_5Cl at a yield of greater than about 50%. In another embodiment of producing SF_5Cl or a compound made using the produced SF_5Cl, the reaction proceeds at a temperature of about 10 to about 200 °C.

[0019] In another embodiment of producing SF_5Cl or a compound made using the produced SF_5Cl, the sulfur reactant is S and the metal fluoride is KF and the admixing occurs at a stoichiometric ratio of about 5KF to about 1 Br_2 to about 1 S to about $3Cl_2$ or the sulfur reactant is SF_4 and the metal fluoride is KF and the admixing occurs at a stoichiometric ratio of about 1KF to about 1 Br_2 to about 1 SF_4 to about $1Cl_2$ or the sulfur reactant is SCl_2 and the metal fluoride is KF and the admixing occurs at a stoichiometric ratio of about 5KF to about 1 Br_2 to about 1 SCl_2 to about $2Cl_2$ and the reaction proceeds at a temperature of about 10 to about 200 °C.

[0020] In another embodiment of producing SF_5Cl or a compound made using the produced SF_5Cl, the metal fluoride is an alkaline earth metal fluoride, an alkali metal fluoride, CsF, RbF, KF, BaF_2, SrF_2 or a mixture thereof and/or the sulfur reactant S, S_2Cl_2, SCl_2, SF_4 or a combination thereof.

[0021] Embodiments disclosed herein also include methods of producing SF_5Br or a compound made using the produced SF_5Br. In one embodiment the method includes admixing a Br_2 reactant, a sulfur reactant, and a metal fluoride reactant thereby initiating a reaction that produces SF_5Br at a yield of greater than about 50%. In another embodiment of producing SF_5Br or a compound made using the produced SF_5Br, either S_2F_{10} or BrF, BrF_3, BrF_5, $CsBrF_4$, $CsBrF_2$ or mixtures thereof are not added to the reaction. In another embodiment of producing SF_5Br or a compound made using the produced SF_5Br, the reaction proceeds at a temperature of about 10 to about 140 °C.

[0022] In another embodiment of producing SF_5Br or a compound made using the produced SF_5Br, the sulfur reactant is SF_4 and the metal fluoride is AgF and the admixing occurs at a stoichiometric ratio of about 1 AgF to about 1 Br_2 to about 1 SF_4 or the sulfur reactant is SF_4 and the metal fluoride is AgF_2 and the admixing occurs at a

stoichiometric ratio of about $2AgF_2$ to about 3 Br_2 to about 4 SF_4 and the reaction proceeds at a temperature of about 10 to about 140 °C.

[0023] In another embodiment of producing SF_5Br or a compound made using the produced SF_5Br, the metal fluoride is an alkaline earth metal fluorides, an alkali metal fluorides, AgF_2, AgF, AuF, MnF_3, PbF_4, CeF_4 or a mixture thereof.

[0024] Embodiments disclosed herein also include methods of producing SF_6 or a compound made using the produced SF_6. In one embodiment, the method includes : admixing a Br_2 reactant, an SF_4 reactant, and a metal fluoride reactant thereby initiating a reaction that produces SF_6 at a yield of greater than about 50%. In another embodiment of producing SF_6 or a compound made using the produced SF_6, the reaction proceeds at a temperature of about 10 to about 400 °C.

[0025] In another embodiment of producing SF_6 or a compound made using the produced SF_6, the sulfur reactant is SF_4 and the metal fluoride is CoF_3 and the admixing occurs at a stoichiometric ratio of about 2 CoF_3 to about 1 Br_2 to about 1 SF_4 and the reaction proceeds at a temperature of about 10 to about 400 °C.

[0026] In another embodiment of producing SF_6 or a compound made using the produced SF_6, the metal fluoride is selected from the group consisting of an alkaline earth metal fluoride, an alkali metal fluoride, CoF_3, MnF_3, PbF_4, CeF4 or a mixture thereof.

DETAILED DESCRIPTION OF THE INVENTION

[0027] Described herein are methods for the synthesis of fluoro-sulfur compounds in the presence of Br_2. In certain exemplary embodiments the fluoro-sulfur compounds are SF_4, SF_5Cl SF_5Br and SF_6. The methods disclosed herein involve the mixing of readily available and relatively inexpensive reactants. When compared to previously-used approaches, the methods described herein generally require lower temperatures and pressure, produce high yields, require less time, do not use excessively reactive or costly reactants and solvents that are frequently utilized in the synthesis of the fluoro-

sulfur compounds, do not produce deleterious waste products or one or more of the above in various combinations.

[0028] Disclosed methods of synthesizing SF_4 utilize Br_2 in both the presence and absence of Cl_2, whereas disclosed methods of synthesizing SF_5Cl utilize Br_2 in the presence of Cl_2. Disclosed methods of synthesizing SF_4 and SF_5Cl can utilize Br_2 in the absence of excessive temperature and pressure, and, in certain embodiments, in the absence of acetonitrile, Dioxane, ClF, ClF_3, NOF, HF, F_2, $(HF)_n$•amine and/or IF_5. Disclosed methods of synthesizing SF_5Br utilize Br_2 and can be carried out in the absence of high reaction temperatures and pressures, and in certain embodiments, in the absence of S_2F_{10}, BrF_3, BrF_5, $CsBrF_4$ and/or $CsBrF_2$. Disclosed methods of synthesizing SF_6 utilize Br_2 and can be carried out in the absence of electrochemical preparation, high reaction temperatures and/or pressures, and, in certain embodiments, in the absence of F_2, SF_5Cl, IF_5, SF_4, ClF and/or HF.

[0029] As used herein “metal fluoride (MF)” encompasses a variety of mono or multivalent MFs including, without limitation, alkaline earth fluorides and alkali metal fluorides and can particularly include, without limitation, CoF_3, CeF_4, MnF_3, PbF_4, CsF, RbF, KF, BaF_2, SrF_2, AgF_2, AgF and AuF.

[0030] As used herein, the term "about" is used to indicate that a value includes the standard deviation of error for the device or method being employed to determine the value.

[0031] In one example embodiment, the synthesis of SF_4 is described. One example synthesis reaction for SF_4 can proceed as follows in reaction I:

$$\text{I. } 4KF + S + 2Br_2 \rightarrow SF_4 + 4KBr$$

[0032] In reaction I, the SF_4-producing reaction can proceed at autogenous or elevated reaction pressures at ambient temperatures of about 10 to about 27 °C, or at a mildly-elevated temperatures of up to about 80 °C, or even at higher temperatures that are below those (about 400 to about 500 °C) which promote SF_4 to disproportionate into S and SF_6. Accordingly, the described methods do not require excessive temperatures or pressures or require the use of unusually reactive or costly reactants or solvents that

are commonly used in the synthesis of SF_4, such as, but not limited to acetonitrile, Dioxane, HF, F_2, Cl_2, $(HF)_n$•amine and IF_5 .

[0033] The described reaction I can produce yields ranging from about 57 to about 96% or greater, in a time frame of several hours to several days. Due to the low cost of the reagents used, modifying the reaction to produce lower yields can also be commercially advantageous. In one embodiment, yields of 10% or higher can be produced.

[0034] This reaction does not create or leave behind undesirable side products. Only Br_2, MFs and sulfur bromides that can easily be removed and discarded or recycled into subsequent production runs of SF_4 or other unrelated chemical reactions, are created. Moreover, the disclosed reaction produces little or no gases, other than SF_4, making purification of the SF_4 end-product a simple process. Particularly, low boiling constituents (S_{F4}) or excess unused Br_2 can be separated by lowering the temperature and transferring into a cold trap.

[0035] This described reaction I provides a method for synthesizing SF_4 employing Br_2 in the absence of Cl_2. The absence of Cl_2 in this reaction prevents the formation of SF_5Cl when SF_4 is the desired SF_4 end-product.

[0036] In another example embodiment, either S, Br_2, or both S and Br_2 can be replaced by sulfur bromides (*e.g.* S_2Br_2, SBr_2) in the production of SF_4. In one embodiment, specifically relating to reaction I, S to Br_2 molar ratios of greater than about 1.00 : 2.00 can be used. In alternative embodiments, ratios ranging from about 1.00 : 0.44 to about 1.00 : 5.33 can also be used. In another example embodiment, particularly useful MFs in the production of SF_4 and SF_5Cl include, without limitation, CsF, RbF, KF, BaF_2, SrF_2 or a combination thereof.

[0037] Further described herein are methods for the production of SF_5Cl, and optionally SF_4 (in the presence of Cl_2), utilizing Br_2 as a solvent and/or reactive solvent. In the case of S as a reactant, when SF_4 is the desired product, slightly more than about four equivalents of the MF can be used. If SF_5Cl is the desired product, slightly more than about five equivalents of the MF can be used. When SF_4 is used as a reactant to produce SF_5Cl, an equivalent or slightly larger amount of the MF can be utilized to

efficiently produce the SF_5Cl. The minimum amount of Cl_2 in the reactions can easily be determined by the stoichiometry of the reaction itself. In the present example embodiment, KF is used as the MF, however, a variety of other mono or multivalent MFs can be used.

[0038] Example synthesis reactions for SF_4 and SF_5Cl in the presence of Cl_2 as described above proceed as follows in reactions II-IV:

$$\text{II.}\quad 4\,KF + S + 2\,Cl_2 + (Br_2) \rightarrow SF_4 + 4\,KCl + (Br_2)$$

$$\text{III.}\quad 5\,KF + S + 3\,Cl_2 + (Br_2) \rightarrow SF_5Cl + 5\,KCl + (Br_2)$$

$$\text{IV.}\quad KF + SF_4 + Cl_2 + (Br_2) \rightarrow SF_5Cl + KCl + (Br_2)$$

[0039] In reactions II-IV above, the SF_5Cl- and SF_4-producing reactions can proceed at autogenous or elevated reaction pressures, at ambient temperatures of about 10 to about 27 °C, or at a mildly-elevated temperatures of up to about 115 °C, or, even at higher temperatures that are below those which promote decomposition of SF_5Cl (about 200 to about 400 °C), or cause SF_4 to disproportionate into S and SF_6 (about 400 to about 500 °C). Accordingly, the described methods do not require excessive temperatures or pressures or require the use of unusually reactive or costly reactants or solvents that are commonly used in the synthesis of SF_4 and SF_5Cl, such as, but not limited to acetonitrile, Dioxane, ClF, ClF_3, NOF, HF, F_2, $(HF)_n$•amine and IF_5 .

[0040] The described reaction III above can produce yields of about 88 to about 95% or greater and can theoretically approach 100%, in a time frame of several hours to several weeks. Due to the low cost of the reagents used, modifying the reaction to produce lower yields can also be commercially advantageous. In one embodiment, yields of 50% or higher can be produced. Other lower yields, such as yields as low as 10%, are also within the scope of embodiments disclosed herein.

[0041] This reaction does not create or leave behind undesirable side products. Br_2 can be easily separated from the reaction products and then SF_5Cl and any excess Cl_2 can be collected by cooling the reaction vessel to approximately -80°C and condensing out SF_5Cl and any excess Cl_2 at reduced pressure. Cl_2 can be removed from the mixture by storage over elemental sulfur and the recovered sulfur chlorides can be used for a

new production batch of either SF_4 or SF_5Cl. One function of the chlorine in the procedure is to oxidize sulfur to sulfur chlorides (*e.g.* S_2Cl_2, SCl_2) as the predominant sulfur species, which exchange chlorine for fluorine with a fluoride. Thus, it will not be necessary to dispose of sulfur chlorides as waste. Collectively, the recovered Cl_2 as well as the recovered sulfur chlorides and Br_2, may be used in a near quantitative fashion, as outlined in the following reactions:

$$\text{V. } 4\ KF + SCl_2 + Cl_2 + (Br_2) \rightarrow SF_4 + 4KCl + (Br_2)$$

$$\text{VI. } 5\ KF + SCl_2 + 2Cl_2 + (Br_2) \rightarrow SF_5Cl + 5KCl + (Br_2)$$

[0042] In the SF_4-producing reaction, a small amount of SF_5Cl may be formed as a by-product. In each of the reactions, the function of Br_2 may be to provide an improved reaction environment with Br_2 possibly acting as a solvent, a reactive solvent or with Cl_2 forming BrCl from the Br_2 + Cl_2 upon mixing. Interestingly, it has been shown previously, that without the addition of Br_2, KF + SF_4 + Cl_2 yields, upon intense heating (about 75 to about 150°C or about 220 to about 300°C) only variable amounts (about 5 to about 80%) of SF_5Cl (Bekker *et al.*, Isw. Akad. Nauk U.S.S.R., Bull. Ser. Chim. 2575, 1970; U.Jonethal, R.Kuschel, K.Seppelt, J. Fl. Chem. 88, 3, 1998). Thus, the Br_2 utilized in the present methods alleviates the requirement for excessive temperature (energy input), and also improves both the yield and the consistency of the yield, as well as the overall ease of production. Moreover, when using S instead of SF_4 as the sulfur source to produce SF_5Cl, the use of Br_2 alleviates both the requirement for SF_4 and excessive temperature, as other methods which do not utilize Br_2 (excess CsF + S + 3 Cl_2 at about 175°C) do not produce meaningful amounts of SF_5Cl.

[0043] The methods described herein employ the use of Br_2 as a solvent or reactive solvent in the production of SF_5Cl and SF_4, which in turn promotes the transfer of both fluorine and chlorine into the production of the SF_5Cl and SF_4 end-products.

[0044] Alternatively, in the SF_5Cl-producing reaction, S and Cl_2 may be replaced by sulfur chlorides (*e.g.* S_2Cl_2, SCl_2) or SF_4, if desired. In both the SF_5Cl - and SF_4 - producing reactions described herein, when there is insufficient Br_2 present, the reactions are either extremely slow or do not progress at all. Further, in both the SF_5Cl - and SF_4-producing reactions that utilize Cl_2 as a reactant, a Br_2 to S molar ratio greater

than about 1:1 can be used. Ratios of from about 1:2 to about 2:1 can also be used. Particularly useful MFs in the production of SF_5Cl and SF_4 include, without limitation, CsF, RbF, KF, BaF_2, SrF_2 and combinations thereof.

[0045] In another example embodiment disclosed herein, the synthesis of SF_5Br is described. In the case where SF_4 and Br_2 are reactants, more than about 1 equivalent of a metal monofluoride (AgF) can be used or about 2 equivalents can be used in the case of a metal difluoride (AgF_2). Example synthesis reactions for SF_5Br can proceed as follows:

$$\text{VII. } AgF + SF_4 + Br_2 \rightarrow SF_5Br + AgBr$$

$$\text{VIII. } 2AgF_2 + 4SF_4 + 3Br_2 \rightarrow 4SF_5Br + 2AgBr$$

These reactions can be run at ambient temperatures (about 10 to about 27 °C) or at temperatures up to those at which SF_5Br begins to decompose (about 140 to about 150 °C) and at the autogenous pressures generated in closed reactor vessels. Highly-reactive and/or costly reactants that are commonly used to synthesize SF_5Br, such as, without limitation, S_2F_{10}, BrF_3, BrF_5, $CsBrF_4$ and $CsBrF_2$ are not necessary.

[0046] The described reaction can produce yields of about 75% and can theoretically approach 100%, in a time frame of several hours to several days. Due to the low cost of the reagents used, modifying the reaction to produce lower yields can also be commercially advantageous. In one embodiment, yields of 50% or higher can be produced. Other lower yields, such as yields as low as 10%, are also within the scope of embodiments disclosed herein.

[0047] The reaction does not create or leave behind undesirable side products. SF_5Br and any excess Br_2 can be collected by cooling the reaction vessel to approximately -78°C and condensing out the SF5Br. The Br_2 can be easily recycled into subsequent reactions including, without limitation, the production of SF_5Br, whereas AgBr can be readily reutilized in subsequent reactions including, without limitation, SF_5Br reactions by reforming the metal fluoride (without limitation, AgF or AgF_2).

[0048] In one example embodiment, the present SF_5Br production methods can employ only SF_4, a MF, for example and without limitation, AgF or AgF_2, and Br_2 as

reactants. Particularly useful MFs in the production of SF_5Br include, without limitation, CeF_4, MnF_3, PbF_4, AgF_2, AgF, AuF or a mixture thereof. Further, the methods described herein for producing SF_5Br eliminate inefficient multi-step production protocols that are currently used.

[0049] In another example embodiment disclosed herein, the synthesis of SF_6 is described. In the case where SF_4 and Br_2 are reactants, more than about 2 equivalents of a MF capable of transferring about one fluorine equivalent, such as CoF_3, can be used. An example synthesis reaction for SF_6 can proceed as follows:

$$\text{IX. } 2CoF_3 + SF_4 + (Br_2) \rightarrow SF_6 + 2CoF_2 + (Br_2)$$

Reaction IX shown above can be run at ambient temperatures or theoretically up to temperatures at which SF_4 begins to decompose (about 400 to about 500 °C), and at the autogenous pressures generated in closed reactor vessels. Electrochemical preparation, high temperatures and pressures as well as highly-reactive and/or costly reactants (without limitation, F_2, SF_5Cl, IF_5, SF_4, ClF and HF) that are commonly used to synthesize SF_6 can be avoided.

[0050] Due to the low cost of the reagents used, modifying the reaction to produce lower yields can also be commercially advantageous. In one embodiment, yields of 50% or higher can be produced. Other lower yields, such as yields as low as 10%, are also within the scope of embodiments disclosed herein.

[0051] In the described reaction IX, the Br_2 can be easily recycled into subsequent reactions including, without limitation, the production of additional SF_6, whereas CoF_2 can be readily re-fluorinated to CoF_3 and reutilized in subsequent SF_6 reactions as well as other reactions.

[0052] In one example embodiment, the present SF_6 production methods can employ only SF_4, a MF, for example and without limitation, CeF4, MnF3, PbF4, AgF_2, AgF, AuF and mixtures thereof as reactants. Further, the methods described herein for producing SF_6 eliminate inefficient multi-step production protocols that are currently used.

[0053] The reactions described herein for producing SF_4, SF_5Cl, SF_5Br and SF_6 can be performed at temperatures below those commonly used in the art. In one example embodiment, the reactions are carried out at or near room (ambient) temperature (about 10 to about 27 °C). In other embodiments, the temperature is from about 10°C to about 27 °C (ambient), or from about 27 °C to about 115 °C. Higher temperatures can theoretically be used, for example, up to about 250 °C to about 500 °C (up to temperatures at which SF_4, SF_5Cl and SF_5Br decompose). Additionally, lower temperatures can be used, for example down to about -10 °C; a temperature at which Br_2 would solidify. While permissible, however, these more extreme reaction temperatures are not required.

[0054] The reactions described herein for producing SF_4, SF_5Cl, SF_5Br and SF_6 can be performed at pressures below those commonly used in the art. In one example embodiment, the reactions are carried out just above atmospheric pressure, at autogenous pressures that are estimated of only up to about 10 atms. In other embodiments, at higher temperatures, the pressure is estimated to be from about 10 atm to about 40 atm. Slightly higher pressures can also be used. For example, it is estimated that up to about 100 atm could be used. Additionally, lower pressures can be used, for example down to about 0.5 atms, or about 0.01 atms, or about 0.001 atms. While permissible, however, these more extreme pressures are not required.

[0055] Further, in some embodiments, the reactions for producing SF_4, SF_5Cl, SF_5Br and SF_6 described herein can be carried out in one or more physical configuration that increases the reaction surface area of the solid phase reactants. For example, the solid phase reactants can be spray-dried, finely dispersed, or otherwise subjected to commonly used methods which increase the surface area. In some example embodiments, the reactants for producing SF_4, SF_5Cl, SF_5Br and SF_6 can be physically or mechanically agitated to aid the reactions. For example, inversion, milling/grinding, ball-milling, stirring, rotation, and the like can be used. Such mechanical agitation methods can minimize MFBr or MFCl formation that can mask the effective MF reaction surface area and slow the progression of desired reactions.

[0056] The methods described herein theoretically can generate SF_4, SF_5Cl, SF_5Br and SF_6 at near 100% yields. In one example embodiment, the yield is between about 57% and about 96%. In another embodiment the yield is about 95% In another embodiment, the yield is about 75%.

[0057] As will be understood by one of ordinary skill in the art, depending on the reactants used and the desired end-products, the conditions of the reaction and the like, the time for a reaction to be substantially complete varies. Substantially complete means a particular reaction is within about 10% of completion, within about 5% of completion or within about 1% or less of completion. Reaction times can be as short as about a few hours to as long as about several days or weeks. In some embodiments, the reactions are substantially complete within less than about 30 days, less than about 17 days, less than about 14 days, less than about 6 days, less than about 4 days, less than about 3 days, less than about 2 days or less than about 1 day. In other embodiments, the reactions are substantially complete within less than about 8 hours, less than about 4 hours or less than about 3 hours.

[0058] Reactions described herein can be modified by those skilled in the art. As such, altering the order of adding and mixing of reactants and reagents, adjusting relative molar ratios of reactants, as well as altering reaction times, temperatures and pressures, to more precisely control specific reaction outcomes, and maximizing the ease and production of the desired end product are within the scope of the present description.

[0059] The following examples are included to demonstrate embodiments of the disclosed methods and processes. It should be appreciated by those of ordinary skill in the art that the techniques disclosed in the examples which follow represent techniques discovered by the inventor to function well in the practice of the present disclosure, and thus can be considered to constitute preferred modes for its practice. However, those of ordinary skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result.

Example 1. Formation of SF_4

[0060] Anhydrous fine grain KF powder (about 5.09 g) was dried in a stainless steel 100-ml Hoke bomb tube reactor at about 150 °C to about 200 °C, for about 1 hour, at high vacuum (about 0.05 to about 0.1 torr). The reactor was allowed to cool to ambient temperature, opened, and fine-grain S powder (about 0.69 g) was added. Cl_2 (about 3.13 g) and Br_2 (about 1.5 g) were then added to the reactor vessel by condensation to produce a molar ratio of S : Cl_2 : KF : Br_2 of about 1.0 : 2.0 : 4.1 : 0.44. The vessel was kept at ambient temperature overnight and little or no SF_5Cl and SF_4 were detected from the infrared (IR) spectrum of the gaseous phase. IR spectrometry was performed using a Model 4020 Galaxy FTIR spectrophotometer (Mattson Instruments, Madison, WI 53711, USA). No change in the IR spectrum was noticed after about four more days. More Br_2 (about 5.5 g) was added to the reactor vessel by condensation to produce a new molar ratio of: S : Cl_2 : KF : Br_2 of about 1 : 2.0 :4.1 : 2.0. After about 4 days at ambient temperature, a very strong SF_4 -specific spectral signal was observed (*e.g.* band groups centered at about 876 cm^{-1} and about 730 cm^{-1}), which was accompanied by a very weak SF_5Cl IR spectral signal (*e.g.* band groups centered at about 909 cm^{-1}, about 855 cm^{-1} and about 602 cm^{-1}), The reaction displayed a high degree of conversion to SF_4, as indicated by the IR spectrum. This example illustrates that: 1.) increasing the molar ratio of Br_2 appears to promote the formation of SF_4, and 2.) SF_4 can be efficiently synthesized within about 4 days at ambient temperatures in the reaction:

$4\ KF + S + 2Cl_2 + (Br_2) \rightarrow SF_4 + 4KCl + (Br_2)$.

Example 2. Formation of SF_4 at an Elevated Temperature

[0061] Anhydrous fine-grain KF powder (about 10.50 g) was dried in a stainless steel 100-ml Hoke bomb tube reactor at about 150 °C to 200 °C, for about 1 hour, at high vacuum. The reactor was allowed to cool to ambient temperature, opened, and fine-grain S powder (about 1.37 g) was added. Cl_2 (about 6.1 g) and Br_2 (about 14.3 g) were then added to the reactor vessel by condensation to produce a molar ratio of S : Cl_2 : KF : Br_2 of about 1.00 : 2.00 : 4.23 : 2.09. The vessel was then kept at a temperature of 65 - 70 °C for 30 days. Initially, some SF_5Cl besides SF_4 was detected

in the IR spectrum of the gaseous constituents of the reactor bomb tube, but it disappeared in the course of time and no SF_5Cl was detected after 30 days, only SF_4. (IR spectrometry was performed). The reactor vessel bomb tube was cooled to -78 °C , and pumped on through a liquid-nitrogen cooled cold trap for two hours. The crude product (4.6 g) was stored in a reactor vessel bomb tube over sulfur (20 g) for 20 hours to remove excess chlorine that might be present. After cooling the sulfur-treatment vessel to -78 °C, the product was collected in a cold trap (liquid nitrogen) as before. A yellow tinge was removed by treatment with Hg. The final mass of the recovered SF_4 end product was about 4.08 g for a calculated yield of about 88% (based upon sulfur). The final SF_4 product appeared as a colorless liquid (when cold), showing the characteristic bands of SF_4 in the IR spectrum. This example illustrates that: 1.) increasing the temperature appears to promote the formation of SF_4, and 2.) SF_4, free of SF_5Cl, can be efficiently synthesized in the reaction:

$$4\ KF + S + 2Cl_2 + (Br_2) \rightarrow SF_4 + 4KCl + (Br_2)$$

Example 3. Alternate Formation of SF_4 in the Absence of Cl_2

[0062] Anhydrous fine-grain KF (about 24.2 g) was dried in a stainless steel 300-ml Hoke bomb tube reactor at about 150 °C to about 200 °C, for about 1 hour, at high vacuum. The reactor was allowed to cool to ambient temperature, opened, and fine-grain S powder (about 3.24g) was added. Br_2, representing a molar ratio of S to Br_2 of greater than about two (about 86.4 g), was then added to the reactor vessel by condensation to produce a final molar ratio of S : KF : Br_2 of about 1.00 : 4.10 : 5.30. After about 3 days at ambient temperature, a strong SF_4 IR spectral signal was observed and the reaction displayed a high degree of conversion to SF_4. After an additional 3 days at ambient temperature, no significant change was noticed in the IR spectrum.

[0063] The final SF_4 product was isolated as follows: The reaction vessel was cooled on a dry ice bath (about -78 °C) and connected via a liquid nitrogen cold trap (about –196 °C) to a vacuum pump. After about 1.5 hours, about 11.5 grams of a light brown, presumably bromine-contaminated crude product was obtained. To remove residual contaminants (*e.g.* Br_2, Sulfur Bromides), the crude product was condensed

into a large glass pressure vessel containing about 10 grams of Hg to remove trace amounts of any discoloring contaminants (*i.e.* e.g. Br_2). After brief shaking at about 0 °C, the product was condensed into a cold trap and obtained as a colorless liquid. The final mass of the recovered end product was about 10.5 g for a calculated yield of about 96% (based upon sulfur). The IR spectrum of the end product revealed a substantially pure sample of SF_4, with a small contamination by SOF_2 (e.g. band groups centered at about 1340 cm^{-1} and about 808 cm^{-1} and about 750 cm^{-1}),. This example illustrates that: SF_4 can be efficiently synthesized in the absence of Cl_2 within about 3 days at ambient temperatures, in the reaction:

$$4KF + S + 2Br_2 \rightarrow SF_4 + 4KBr$$

Example 4. Alternate Formation of SF_4 Using Coarse-grain KF and Agitation by Ball-milling

[0064] Anhydrous coarse grain KF (about 28.1 g) was dried in a stainless steel 300-ml Hoke bomb tube reactor containing 19, ½ inch 316 grade stainless steel balls, at about 150 °C to about 200 °C, for about 1 hour, at high vacuum. The reactor was allowed to cool to ambient temperature, opened, and fine-grain S powder (about 3.8g) was added. Bromine, (about 63.1 g), was then added to the reactor vessel to produce a final molar ratio of S : KF : Br_2 of about 1.00 : 4.10 : 3.30. After rotating the reaction vessel for about 4 days at ambient temperature, a strong SF_4 IR spectral signal was observed and the reaction displayed a high degree of conversion to SF_4.

[0065] The final SF_4 product was isolated as follows: The reaction vessel was cooled to about -78 °C and connected via a cold trap (about –196 °C) to a vacuum pump. After about 5 hours, about 9.8 grams of a light brown, presumably bromine-contaminated crude product was obtained. A low temperature vacuum transfer was performed, yielding a very light brown liquid. The final mass of the recovered SF_4 end product was estimated about 7.3 g for a calculated yield of about 57% (based upon sulfur). The IR spectrum of the end product revealed a substantially pure sample of SF_4, with a small contamination by SOF_2. This example illustrates that: SF_4 can be efficiently synthesized in the absence of Cl_2 using coarse-grain KF and ball-milling agitation within about 4 days at ambient temperatures, in the reaction:

$4KF + S + 2Br_2 \rightarrow SF_4 + 4KBr$

Example 5. Alternate Formation of SF_4 at Elevated Temperature

[0066] Anhydrous fine-grain KF (about 17.1 g) was dried in a stainless steel 300-ml Hoke bomb tube reactor at about 150 °C to about 200 °C, for about 1 hour under high vacuum. The reactor was allowed to cool to ambient temperature, opened, and fine-grain S powder (about 2.3g) was added. Br_2 (about 36.3 g), was then added to the reactor vessel to produce a final molar ratio of S : KF : Br_2 of about 1.00 : 4.10 : 3.20. The reactor vessel was heated to about 60 °C for about 3 hours and the formation SF_4 product was monitored by IR spectroscopy. The reaction vessel was cooled to about -78 °C and the SF_4 product was pumped into a liquid nitrogen cold trap. The mass of the crude SF_4 product indicated about 50% chemical yield. After recondensation of the SF_4 product into the reaction vessel, it was heated for another about 2 hours at about 72 °C, and another about 4 hours at about 80 to about 86 °C. Isolation of the SF_4 product was accomplished by cooling the reaction vessel to about -78 °C and pumping under high vacuum for about 1.5 hours into a liquid nitrogen cold trap. Debromination was performed by brief shaking in large Carius tube containing about 20 g. of Hg at about 0 °C. About 6.7 grams of purified SF_4 was recovered containing a small amount of SOF_2, as judged by IR spectroscopy. The final calculated yield was about 86% (based upon sulfur). This example illustrates that SF_4 can be efficiently synthesized at mildly elevated temperature, within about 9 hours, in the reaction:

$4KF + S + 2Br_2 \rightarrow SF_4 + 4KBr$

Example 6. Alternate Formation of SF_4 While Limiting Br_2

[0067] Anhydrous fine grain KF (about 24.12 g) was dried in a stainless steel 300-ml Hoke bomb tube reactor at about 150 °C to about 200 °C, for about 1 hour, at high vacuum. The reactor was allowed to cool to ambient temperature, opened, and fine-grain S powder (about 3.16 g) was added. Br_2 (about 31.1 g), was then added to the reactor vessel to produce a final molar ratio of S : KF : Br_2 of about 1.00 : 4.21 : 1.97. The reaction vessel was then cooled with liquid nitrogen and evacuated. The reaction vessel was kept at ambient temperature for about 6 days, and then heated at about 80 °C for about 8 hours. The reaction vessel was cooled to about -78 °C and the volatile

material was pumped into a liquid nitrogen cooled cold trap until transfer apparently ceased. The contents of the cold trap were transferred to a second cold trap, leaving a brown residue in the first cold trap. The transferred material was condensed into a large glass pressure vessel containing about 10 grams of Hg to remove trace amounts of. Br_2. About 7.31 g of colorless product was again condensed into a liquid nitrogen cooled cold trap. The recovered end product appeared as colorless product of about 7.31 g mass, for a calculated yield of about 70% (based upon Br_2). The IR spectrum of the end product revealed a substantially pure sample of SF_4. This example illustrates that it is advantageous to use more than the required stoichiometric amount of bromine in the reaction:

$4KF + S + 2Br_2 \rightarrow SF_4 + 4KBr$

Example 7. Formation of SF_5Cl

[0068] Anhydrous fine grain CsF (about 10.95 g) was dried under high vacuum at about 100 °C in a stainless steel 300-ml Hoke bomb tube reactor, whereupon SF_4 (about 9.17 g), Cl_2 (about 3.20 g) and bromine (about 36.8 g) were added consecutively by vacuum condensation at liquid-nitrogen temperature (about –196 °C) to produce a molar ratio of SF_4 : CsF : Cl_2 : Br_2 of about 1.00 : 0.85 : 0.53 : 2.71. The vessel was set aside at ambient temperature for about 5 days, and an IR spectrum of the gaseous constituents showed very strong bands or band groups corresponding to SF_5Cl. This example illustrates that SF_5Cl can be efficiently synthesized within about 5 days at ambient temperatures using Cl_2 , Br_2, and SF_4, in the reaction:

$CsF + SF_4 + Cl_2 + (Br_2) \rightarrow SF_5Cl + CsCl + (Br_2)$.

Example 8. Alternate Formation of SF_5Cl Using a Different Metal Fluoride

[0069] KF (about 5.0 g) was dried at about 150 °C to about 200 °C in a stainless steel 100-ml Hoke bomb tube reactor, for about 1 hour, at high vacuum. Br_2 (about 9.71 g), Cl_2 (about 3.54 g) and SF_4 (about 4.71 g) were added to the bomb tube reactor by condensation to produce a molar ratio of: SF_4 : Cl_2 : KF : Br_2 of about 1.00 : 1.14 : 1.98 : 1.39. The reaction appeared almost complete after about 2 days at ambient temperature, as determined from the IR spectrum (*i.e.* a strong SF_5Cl to SF_4 IR spectral

signals was observed). The reactants were then heated for about 2 days at about 115°C, and an IR spectrum of the gaseous phase showed very little signal corresponding to SF_4. This example illustrates that SF_5Cl can be efficiently synthesized within about 2 to about 4 days at ambient or mildly elevated temperatures using Cl_2 , Br_2, and SF_4, in the reaction:

$KF + SF_4 + Cl_2 + (Br_2) \rightarrow SF_5Cl + KCl + (Br_2)$.

Example 9. Alternate Formation of SF_5Cl Using S Instead of SF_4

[0070] KF (about 15.60 g) was added to a stainless steel 300-ml Hoke bomb tube reactor and dried at about 150 °C to about 200 °C, for about 1 hour, at high vacuum. The bomb reactor was opened and fine-grain S powder (about 1.50 g) was added. After resealing the reactor, Cl_2 (about 9.03 g) and Br_2 (about 8.59 g) were added by condensation to produce a molar ratio of : S : Cl_2 : KF : Br_2 of about 1.00 : 2.71 : 5.71 : 1.15. The pressure reactor was kept at ambient temperature overnight and both SF_5Cl and SF_4 were detected from the IR spectrum. No change in the IR spectrum was noticed after about three days. More Cl_2 was added (about 1.20 g), bringing the molar ratio to: S : Cl_2 : KF : Br_2 of about 1.00 : 3.26 : 5.72 : 1.15. The reaction was occasionally monitored by IR spectroscopy. After about two more weeks at ambient temperature, the reaction was substantially complete as judged by IR spectrometry. This example illustrates that 1.) compared to other SF_4-producing reactions, increasing the molar ratios of Cl_2 and KF promotes the production of SF_5Cl over SF_4 in this reaction, and 2.) SF_5Cl can be efficiently synthesized, at ambient temperatures within weeks, in the reaction: $5KF + S + 3Cl_2 + (Br_2) \rightarrow SF_5Cl + 5KCl$.

Example 10. Formation of SF_5Cl

[0071] KF (about 10.55 g) was dried under high vacuum in a stainless steel 100-ml Hoke bomb tube reactor and dried for about 1 hour at about 150 °C to about 200 °C. The reactor was opened and fine-grain S powder (about 1.13 g) was added. After resealing the reactor, Cl_2 (about 8.15 g) and Br_2 (about 7.99 g) were added by condensation to produce a stoichiometric ratio of S : Cl_2 : KF : Br_2 of about 1.00 : 3.25 :5.15 : 1.41 (reaction "A"). A second, similar reaction was prepared utilizing about 1.58 g of fine-grain S powder and the same molar ratios of the other constituents (reaction

"B"). The reaction "A" and "B" vessels were placed at ambient temperature for about 3 days and the successful production of SF_4 and SF_5Cl was noted by IR spectroscopy. Thereafter, SF_4 and SF_5Cl were monitored every 2 to about 3 days by IR spectroscopy, and by about day 13, it was evident that the reaction was not at completion, and that the production of SF_4 and SF_5Cl had slowed significantly. The volatile components of both reaction vessels were then condensed and combined into a third vessel containing about 7.94 grams of KF. After about 4 more days at ambient temperature, IR spectroscopy revealed that all the remaining SF_4 appeared to have been consumed, leaving SF_5Cl as the apparent sole product.

[0072] The final product was isolated in the following manner: 1.) The reaction vessel was cooled to about -78 °C and connected via a cold trap (about –196° °C) to a vacuum pump. After about 6 hours, about 15.5 grams of a light yellowish crude product was obtained. To remove residual contaminants (*e.g.* Cl_2, Br_2, Sulfur Chlorides), the crude product was kept overnight in a pressure reactor, over about 3 grams of S. The product was pumped out of this vessel, cooled to about -78 °C and connected via a cold trap (about –196 °C) to a pump and then condensed into a large cold trap containing a small amount of mercury to remove trace amounts of any discoloring contaminants (*e.g.* Br_2, Sulfur Chlorides). The product was obtained as a colorless liquid. The final mass of the recovered end product was about 13.10 g for a calculated yield of about 95% (based upon Sulfur). The IR spectrum of the end product revealed a pure sample of SF_5Cl.

[0073] This example illustrates that 1.) Additional KF may be required to recharge the SF_5Cl-producing reaction and drive it to completion or near completion. 2.) The production of SF_5Cl may be slowed by a reduction of reaction-accessible KF, perhaps due to the buildup of unreactive KCl on the exposed surfaces of the KF; which may be rectified by the addition of fresh KF, agitation of the reaction vessel, or other methods that may increase reactive surface area of the KF over the reaction time. 3.) From the reaction: $5KF + S + 3Cl_2 + (Br_2) \rightarrow SF_5Cl + 5KCl + (Br_2)$ it is possible to reach complete, or substantially complete SF_5Cl production within about 2 to about 3 weeks at ambient temperature, yielding substantially pure SF_5Cl.

Example 11. Formation of SF_5Cl

[0074] KF (about 10.58 g) was dried under high vacuum for about 1 hour at about 150 °C to about 200 °C, in a stainless steel 300-ml Hoke bomb tube pressure reactor. The reactor was opened and S (about 1.1 g) was added. After resealing the reactor, Cl_2 (about 9.0 g) was added by condensation to produce a stoichiometric ratio of S : Cl_2 : KF of about 1.00 : 3.70 : 5.30. The reaction vessel was set aside at ambient temperature and no production of either SF_4 or SF_5Cl was detected by IR spectroscopy after about 30 days. Br_2 (about 7.54 g) was then added by condensation to produce a new stoichiometric ratio of S : Cl_2 : KF : Br_2 of about 1.00 : 3.70 : 5.30 : 1.37. After about 3 days at ambient temperature, production of both SF_4 and SF_5Cl was noted by IR spectroscopy. This example illustrates that 1.) Although all the chemical elements required for production of SF_4 and SF_5Cl were present in the reaction vessel for a duration of about 30 days, no production of SF_4 or SF_5Cl was noted in the absence of Br_2 at ambient temperature. 2.) After the necessary components (S, Cl_2, KF) of the reaction remained unreactive for 30 days, the subsequent addition of Br_2, within days, promoted the efficient formation of SF_4 and SF_5Cl at ambient temperatures. 3.) Br_2 appears to be required for the efficient ambient temperature production of SF_4 and SF_5Cl from the reactants KF, S and Cl_2.

Example 12. Formation of SF_5Br

[0075] AgF (about 11.02 g) was dried under high vacuum at about 150 to about 200 °C. Br_2 (about 35.5 g) and SF_4 (about 7.3g) were added to a 300-ml Hoke bomb tube pressure reactor by condensation to produce a molar ratio of: SF_4 : AgF : Br_2 of about 1.00 : 1.28 : 3.30. The reaction vessel was then placed into an about 100 °C boiling water bath and subsequently monitored by IR spectroscopy at about 2, about 6.5, about 15 and about 79 hours. The IR spectra indicated a progressive accumulation of SF_5Br (*e.g.* band groups centered at about 891cm $^{-1}$ and about 854 cm $^{-1}$ and about 594 cm $^{-1}$), and a reduction in SF_4, as exemplified by observing an increasing ratio of SF_5Br to SF_4 IR spectral signals over time.

[0076] The final product was isolated in the following manner: The reaction vessel was cooled to about -78 °C and connected via a cold trap (about –196 °C) to a vacuum

pump. After about 3 hours, about 9.3 grams of a light yellowish crude product was obtained in the cold trap. The product was vacuum transferred from the cold trap to a Carius tube containing a small amount of mercury to remove trace amounts of any discoloring contaminants (*e.g.* Br_2). The product was obtained as a pale straw-yellow liquid. The final mass of the recovered end product was about 8.55 g for a calculated yield of about 75.4% (based upon SF_4). The IR spectrum of the end product revealed a substantially pure sample of SF_5Br. This example illustrates that: 1.) SF_5Br can be efficiently synthesized within about 79 hours at 100 °C in the reaction:

$$AgF + SF_4 + Br_2 \rightarrow SF_5Br + AgBr$$

Example 13. Formation of SF_5Br Using an Alternate Metal Fluoride

[0077] AgF_2 (about 2.33 g) was dried under high vacuum at about 150 to about 200 °C in a 100-ml Hoke bomb tube pressure reactor. Br_2 (about 12.95 g) and SF_4 (about 3.14g) were added to the reactor by condensation to produce a molar ratio of: SF_4 : AgF_2 : Br_2 of about 1.00 : 0.55 :2. 78. The reaction vessel was then placed at 100 °C and subsequently monitored by IR spectroscopy at about 52 hours. The IR spectrum indicated very strong bands or band groups indicative of SF_5Br, very weak bands or band groups corresponding to SF_4 and SOF_2 and medium-strength bands or band groups corresponding to SF_6 (e.g. medium-strength band centered at about 947 cm^{-1}). This example illustrates that: 1.) SF_5Br can be efficiently synthesized within about 52 hours at about 100 °C in the reaction:

$$2AgF_2 + 4SF_4 + 3Br_2 \rightarrow 4SF_5Br + 2AgBr$$

Example 14. Formation of SF_6

[0078] CoF_3 (about 4.2 g) was dried under high vacuum at about 150 to about 200 °C in a 100-ml Hoke bomb tube pressure reactor. Br_2 (about 22.0 g) and SF_4 (about 4.63g) were added to the pressure reactor by condensation to produce a molar ratio of: SF_4 : CoF_3 : Br_2 of about 1.00 : 0.84 : 3.21. The reaction vessel was then placed at about 100 °C and subsequently monitored by IR spectroscopy at about 52 hours. The IR spectrum indicated strong bands or band groups indicative of SF_6 moderate-strength bands or band groups corresponding to SF_4 and weak bands or band groups

corresponding to SOF_2. No indication of SF_5Br was evident form the IR spectrum. This example indicates that: 1.) SF_6 can be efficiently synthesized within about 52 hours at about 100 °C in the reaction:

$$2CoF_3 + SF_4 + (Br_2) \rightarrow SF_6 + 2CoF_2 + (Br_2)$$

Example 15. Comparative Example

[0079] To determine if an alternate MF could efficiently replace KF as a reactant in the production of SF4, anhydrous fine-grain NaF (about 16.94 g) was dried in a stainless steel Hoke bomb tube pressure reactor at about 150 °C to about 200 °C, for about 1 hour, at high vacuum. The reactor was allowed to slowly cool to ambient temperature, opened, and sulfur (about 2.17g) was added. Br_2 (about 29.5 g), was then added to the reactor vessel to produce a final molar ratio of S : NaF : Br_2 of about 1.00 : 5.90 : 2.70. After about 2 days at ambient temperature, no SF_4 was evident as measured by IR spectroscopy of the gaseous constituents removed from the reaction vessel. The reaction vessel was then heated to about 80 ^oC for about 18 hours, IR spectroscopy of the gaseous constituents again revealed that no reaction products (SF_4, SOF_2) were present. The reaction vessel was subsequently heated to about 155 ^oC for about 18 hours, IR spectroscopy of the gaseous constituents revealed very low levels SOF_2 and no SF_4, suggesting the formation of only traces of SF_4, which were apparently hydrolyzed by the minuscule amount of water introduced into the reaction vessel.

Example 16. Comparative Example

[0080] To determine if an alternate MF could efficiently replace KF as reactant in the production of SF_5Cl from SF_4, a 100-ml stainless steel Hoke bomb tube reactor was charged with NaF (about 10.19 g), and after drying under high vacuum as described above, the reactor was then charged with chlorine (about 4.77 g), bromine (about 11.57 g) and SF_4 (about 14.61 g), consecutively, by vacuum condensation. The molar ratio of SF_4 : NaF : Cl_2 : Br_2 equaled about 1.00 : 1.79 : 1.10 : 1.50. The reaction was allowed to occur without agitation at ambient temperature for about 11 days , after which time no reaction was apparent from the IR spectrum. Heating of the reaction vessel for an

additional about 9 days at about 115 to about 125 °C did not result in the formation of SF_5Cl, as indicated by IR spectroscopy.

Example 17. Comparative Example

[0081] CuF_2 (about 4.59 g) was dried for about 1 hour under high vacuum at about 150 to about 200 °C. Br_2 (about 18.9 g) and SF_4 (about 3.21 g) were added to the pressure reactor by condensation to produce a molar ratio of: SF_4 : CuF_2 : Br_2 of about 1.00 : 1.54 : 3.72. The reaction vessel was then placed at about 100 °C and subsequently monitored by IR spectroscopy at about 52 hours. The IR spectrum indicated that no reaction had occurred.

Example 18. Comparative Example

[0082] TlF (about 4.23 g) was dried under high vacuum at about 150 to about 200 °C, for about 1 hour. Br_2 (about 7.6 g) and SF_4 (about 1.38 g) were added to the pressure reactor by condensation to produce a molar ratio of: SF_4 : TlF : Br_2 of about 1.00 : 1.49 : 3.86. The reaction vessel was then placed at 100 °C and subsequently monitored by IR spectroscopy at about 52 hours. The IR spectrum indicated that no reaction had occurred.

[0083] Unless otherwise indicated, all numbers expressing quantities of ingredients, properties such as molecular weight, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

[0084] The terms "a," "an," "the" and similar referents used in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. Recitation of ranges of values herein is merely intended to serve as a shorthand method of referring individually to each separate value falling within the range. Unless otherwise indicated herein, each individual value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (*e.g.*, "such as") provided herein is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention otherwise claimed. No language in the specification should be construed as indicating any non-claimed element essential to the practice of the invention.

[0085] Groupings of alternative elements or embodiments of the invention disclosed herein are not to be construed as limitations. Each group member may be referred to and claimed individually or in any combination with other members of the group or other elements found herein. It is anticipated that one or more members of a group may be included in, or deleted from, a group for reasons of convenience and/or patentability. When any such inclusion or deletion occurs, the specification is deemed to contain the group as modified thus fulfilling the written description of all Markush groups used in the appended claims.

[0086] Certain embodiments of this invention are described herein, including the best mode known to the inventors for carrying out the invention. Of course, variations on these described embodiments will become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventor expects skilled artisans to employ such variations as appropriate, and the inventors intend for the invention to be practiced otherwise than specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.

[0087] Furthermore, numerous references have been made to patents and printed publications throughout this specification. Each of the above-cited references and printed publications are individually incorporated herein by reference in their entirety.

[0088] In closing, it is to be understood that the embodiments of the invention disclosed herein are illustrative of the principles of the present invention. Other modifications that may be employed are within the scope of the invention. Thus, by way of example, but not of limitation, alternative configurations of the present invention may be utilized in accordance with the teachings herein. Accordingly, the present invention is not limited to that precisely as shown and described.

What is claimed is:

1. A method of producing a fluoro-sulfur compound or a compound made using said produced fluoro-sulfur compound comprising: admixing Br_2, a metal fluoride reactant, and a sulfur reactant thereby initiating a reaction that produces a yield of said fluoro-sulfur compound of greater than about 10%.

2. A method according to claim 1 wherein said admixing further includes Cl_2.

3. A method according to claim 1 wherein said producing of said reaction proceeds at a temperature of about 10 to about 400°C.

4. A method according to claim 1 wherein either S_2F_{10} or BrF, BrF_3, BrF_5, $CsBrF_4$, $CsBrF_2$, acetonitrile, Dioxane, ClF, ClF_3, NOF, HF, F_2, $(HF)_n$•amine, IF_5 or combinations thereof are not added to said reaction.

5. A method of producing SF4 or a compound made using said produced SF_4 comprising: admixing a sulfur reactant, a metal fluoride reactant, and a Br_2 reactant thereby initiating a reaction that produces SF_4 at a yield of greater than about 10%.

6. A method according to claim 5, wherein said reaction proceeds at a temperature of about 10 to about 400 °C.

7. A method according to claim 5, wherein said sulfur reactant is S and said metal fluoride is KF and wherein said admixing occurs at a stoichiometric ratio of about 4KF to about $2Br_2$ to about 1 S and wherein said reaction proceeds at a temperature of about 10 to about 400 °C.

8. A method according to claim 5, wherein said metal fluoride is an alkaline earth metal fluoride, an alkali metal fluoride, CsF, RbF, KF, BaF_2, SrF_2 or a combination

thereof and/or wherein said sulfur reactant is S, S_2Cl_2, SCl_2, S_2Br_2, SBr_2 or a combination thereof.

9. A method of producing SF_4 or a compound made using said produced SF_4 comprising: admixing a sulfur reactant, a metal fluoride reactant, a Cl_2 reactant and a Br_2 reagent thereby initiating a reaction that produces SF_4 at a yield of greater than about 10%.

10. A method according to claim 9 wherein said reaction proceeds at a temperature of about 10 to about 400 °C.

11. A method according to claim 9 wherein said sulfur reactant is S and said metal fluoride is KF and wherein said admixing occurs at a stoichiometric ratio of about 4KF to about 1 Br_2 to about 1 S to about $2Cl_2$ or wherein said sulfur reactant is SCl_2 and said metal fluoride is KF and said admixing occurs at a stoichiometric ratio of about 4KF to about 1 Br_2 to about 1 SCl_2 to about 1 Cl_2 and wherein said reaction proceeds at a temperature of about 10 to about 400 °C.

12. A method according to claim 9, wherein said metal fluoride is an alkaline earth metal fluoride, an alkali metal fluoride, CsF, RbF, KF, BaF_2, NaF, SrF_2 or a combination thereof and/or said sulfur reactant is S, S_2Cl_2, SCl_2, S_2Br_2, SBr_2 or a combination thereof.

13. A method for producing SF_5Cl or a compound made using said produced SF_5Cl comprising: admixing a Cl_2 reactant, a sulfur reactant, a metal fluoride reactant, and Br_2 reagent thereby initiating a reaction that produces said SF_5Cl at a yield of greater than about 50%.

14. A method according to claim 13 wherein said reaction proceeds at a temperature of about 10 to about 200 °C.

15. A method according to claim 13 wherein said sulfur reactant is S and said metal fluoride is KF and wherein said admixing occurs at a stoichiometric ratio of about 5KF to about 1 Br_2 to about 1 S to about $3Cl_2$ or wherein said sulfur reactant is SF_4 and said metal fluoride is KF and wherein said admixing occurs at a stoichiometric ratio of about 1KF to about 1 Br_2 to about 1 SF_4 to about $1Cl_2$ or wherein said sulfur reactant is SCl_2 and said metal fluoride is KF and wherein said admixing occurs at a stoichiometric ratio of about 5KF to about 1 Br_2 to about 1 SCl_2 to about $2Cl_2$ and wherein said reaction proceeds at a temperature of about 10 to about 200°C.

16. A method according to claim 13, wherein said metal fluoride is an alkaline earth metal fluoride, an alkali metal fluoride, CsF, RbF, KF, BaF_2, SrF_2 or a mixture thereof and/or wherein said sulfur reactant S, S_2Cl_2, SCl_2, SF_4 or a combination thereof.

17. A method for producing SF_5Br or a compound made using said produced SF_5Br comprising: admixing a Br_2 reactant, a sulfur reactant, and a metal fluoride reactant thereby initiating a reaction that produces SF_5Br at a yield of greater than about 50%.

18. A method according to claim 17 wherein either S_2F_{10} or BrF, BrF_3, BrF_5, $CsBrF_4$, $CsBrF_2$ or mixtures thereof are not added to said reaction.

19. A method according to claim 17 wherein said reaction proceeds at a temperature of about 10 to about 140 °C.

20. A method according to claim 17 wherein said sulfur reactant is SF_4 and said metal fluoride is AgF and wherein said admixing occurs at a stoichiometric ratio of about 1 AgF to about 1 Br_2 to about 1 SF_4 or wherein said sulfur reactant is SF_4 and said metal fluoride is AgF_2 and wherein said admixing occurs at a stoichiometric ratio of about $2AgF_2$ to about 3 Br_2 to about 4 SF_4 and wherein said reaction proceeds at a temperature of about 10 to about 140 °C.

21. A method according to claim 17, wherein the metal fluoride is an alkaline earth metal fluorides, an alkali metal fluorides, AgF_2, AgF, AuF, MnF_3, PbF_4, CeF_4 or a mixture thereof.

22. A method for producing SF_6 or a compound made using said produced SF_6 comprising: admixing a Br_2 reactant, an SF_4 reactant, and a metal fluoride reactant thereby initiating a reaction that produces SF_6 at a yield of greater than about 50%.

23. A method according to claim 22 wherein said reaction proceeds at a temperature of about 10 to about 400 °C.

24. A method according to claim 22 wherein said sulfur reactant is SF_4 and said metal fluoride is CoF_3 and wherein said admixing occurs at a stoichiometric ratio of about 2 CoF_3 to about 1 Br_2 to about 1 SF_4 and wherein said reaction proceeds at a temperature of about 10 to about 400 °C.

25. A method according to claim 22, wherein said metal fluoride is selected from the group consisting of an alkaline earth metal fluoride, an alkali metal fluoride, CoF_3, MnF_3, PbF_4, CeF4 or a mixture thereof.