

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
15 June 2006 (15.06.2006)

PCT

(10) International Publication Number
WO 2006/063241 A2

(51) International Patent Classification:

C07C 17/158 (2006.01) C07C 17/361 (2006.01)
C07C 17/20 (2006.01) C07C 19/16 (2006.01)

(21) International Application Number:

PCT/US2005/044638

(22) International Filing Date:

9 December 2005 (09.12.2005)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

11/007,919 9 December 2004 (09.12.2004) US

(71) Applicant (for all designated States except US): **HONEYWELL INTERNATIONAL INC.** [US/US]; 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07960 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **MUKHOPADHYAY, Sudip** [IN/US]; 20 Peabody Street, Buffalo, NY 14210 (US). **HSUEHSUNG, Tung** [US/US]; 16 Vassar Drive, Getzville, NY 14068 (US).

(74) Agent: **HOIRIIS, David**; Honeywell International Inc., 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07960 (US).

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

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: DIRECT ONE-STEP SYNTHESIS FROM CF₃-I

(57) Abstract: The present invention provides a process for the preparation of trifluoromethyl iodide. The process includes the step of: contacting in a reactor a compound represented by the formula: CF₃-W and a compound represented by the formula: Z-I wherein W is selected from CF₃, hydrogen and bromine; Z is selected from hydrogen, iodine and chlorine. The step of contacting is carried out, optionally in the presence of a catalyst and further optionally in the presence of air, at a temperature, pressure and for a length of time sufficient to produce the trifluoromethyl iodide.



WO 2006/063241 A2

DIRECT ONE-STEP SYNTHESIS OF CF₃-I

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

The present invention generally relates to a process for the preparation of trifluoromethyl iodide. More particularly, the present invention relates to a process for the preparation of trifluoromethyl iodide from CF₃-W and Z-I wherein W is CF₃, hydrogen or bromine and Z is hydrogen, iodine or chlorine.

2. DESCRIPTION OF THE PRIOR ART

An article by Dhooge et al. in Proceedings of the 4th Conference on Aerospace Materials, Processes, and Environmental Technology, page 259-268 (2000), describes vapor phase production process for the preparation of CF₃I by the reaction between CHF₃ with I₂ in the presence of a catalyst including alkali metal salts supported on an activated carbon carrier. The reaction mechanism appears to proceed via CF₂ carbenes formed on the catalyst surface as intermediates, followed by carbene disproportionation to CF₃ radicals, followed by reaction with I₂ to give CF₃I (see Nagasaki, Noritaka et al., Catalysis Today (2004), 88(3-4), 121-126).

JP 52068110 (1977) describes the preparation of CF₃I by vapor-phase reaction of Freon 23 with iodine in the presence of alkali or alkaline earth metal salts.

DE 1805457 (1970) describes the preparation of CF₃I and C₂F₅I from the reaction of corresponding bromides and KI without solvent.

Naumann et al., J. Fluorine Chem., **67**(1), 91-3(1994) describes the preparation of CF_3I from CF_3Br by a multi-step reaction, which employs elemental Zn.

European Patent Application EP 266,281 A1 (1988) describes the preparation of CF_3I from CF_3Br by contact with a metal or an alkali metal dithionite and SO_2 followed by treatment with iodine in a carboxylic or sulfonic acid.

Lee, K.-H. et al., Hwahak Konghak, **39**(2), 144-149 (2001) describes the preparation of CF_3I by iodination of $\text{CF}_3\text{CO}_2\text{H}$ with iodine using a flow reactor over various salt-impregnated catalysts.

Su, D. et al., J. Chem. Soc., Chem. Commun. (11), 807-8(1992) describes the preparation of CF_3I by treatment of $\text{XCF}_2\text{CO}_2\text{Me}$ ($\text{X} = \text{Cl}$ or Br) with iodine in the presence of potassium fluoride and copper (I) iodide.

Chiriac, M. et al., Inst. Tehnol. Izot. Mol., **33**(11), 1018-20 (1982) describes the preparation of CF_3I from Ag-trifluoroacetate.

However, in view of the high cost of the raw materials required and the formation of solid by-products that are difficult to dispose of because of their adverse impact on the environment, none of these methods provide a practical and economical process which could be adapted to large scale process for the preparation of CF_3I .

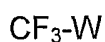
Furthermore, there is no report in the literature of any catalytic vapor-phase process for making CF_3I in high yield. Therefore, a high yield, catalytic vapor-phase process, which avoids the formation of solid by-products and the adverse impact of such solid by-products on the environment would be welcome by the Chemical Industry.

The above described problems can be avoided by the use of a process for the preparation of trifluoromethyl iodide from $\text{CF}_3\text{-W}$ and Z-I wherein W is CF_3 , hydrogen or bromine and Z is hydrogen, iodine or chlorine according to the present invention.

SUMMARY OF THE INVENTION

In broad concept, the present invention provides a process for the preparation of trifluoromethyl iodide. The process includes the step of:

contacting in a reactor a compound represented by the formula:



and a compound represented by the formula:



wherein W is selected from CF_3 , hydrogen and bromine; Z is selected from hydrogen, iodine and chlorine. The step of contacting is carried out, optionally in the presence of a catalyst and further optionally in the presence of air, at a temperature, pressure and for a length of time sufficient to produce the trifluoromethyl iodide.

The present invention has the advantage of providing high yields and high purity trifluoromethyl iodide while avoiding the formation of solid by-products and their adverse impact on the environment.

These and other benefits of the present process will become more evident from the detailed description of the invention that follows.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a process for the preparation of trifluoromethyl iodide from $\text{CF}_3\text{-W}$ and Z-I wherein W is CF_3 , hydrogen or bromine and Z is hydrogen, iodine or chlorine.

CF_3I is a non-toxic, non-flammable, low global warming potential compound with almost zero ozone depletion potential (See, for example, Dhooze et al., Proceedings of the 4th Conference on Aerospace Materials, Processes, and Environmental Technology, page 259-268 (2000)).

In addition, the life cycle of the CF_3I in the atmosphere is only about two days. Therefore, the Chemical Industry has a substantial incentive to produce this compound by a low-cost and environmentally acceptable route for use as a refrigerant either alone or in combination with other known or existing refrigerants.

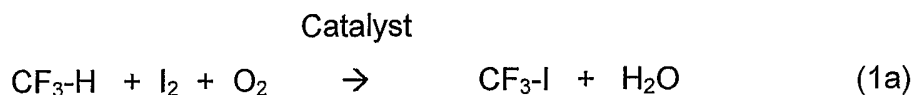
Accordingly, the present invention provides a catalytic process, which uses low cost feedstocks, such as, CHF_3 and Iodine or Hydrogen Iodide as the starting materials to produce CF_3I with high selectivity.

As mentioned herein above, the processes described in the prior art generally are limited to lab-scale demonstration. Furthermore, the raw materials used in these methods are not readily available or expensive. Therefore, a substantial incentive exists for the development of alternative commercial processes for the manufacture of CF_3I .

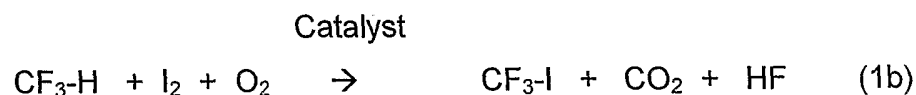
Accordingly, the present invention provides herein a commercially useful catalytic process to achieve these objectives.

Preferred Embodiments:

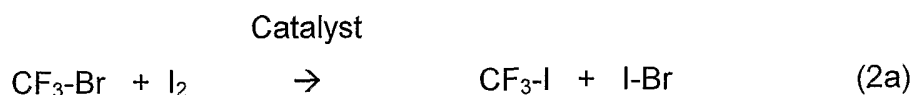
In a one preferred embodiment, W is hydrogen and Z is iodine (1a and 1b), wherein the process proceeds at least in part according to the following equation:



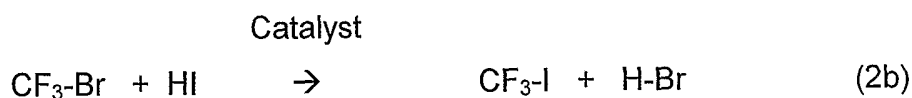
or at least in part according to the following equation:



In another preferred embodiment, W is bromine and Z is iodine (2a), wherein the process proceeds according to the following equation:



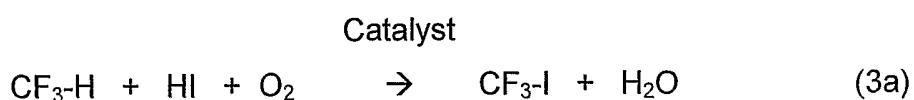
In still another preferred embodiment, W is bromine and Z is hydrogen (2b), wherein the process proceeds according to the following equation:



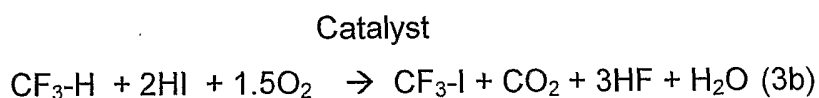
In yet another preferred embodiment, W is bromine and Z is chlorine (2c), wherein the process proceeds according to the following equation:



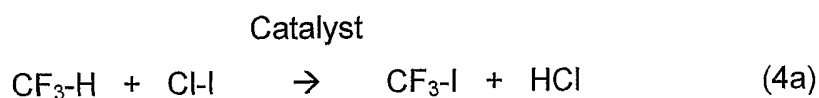
In still another preferred embodiment, W is hydrogen and Z is hydrogen (3a or 3b), wherein the process proceeds at least in part according to the following equation:



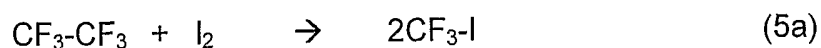
or according to the following equation:



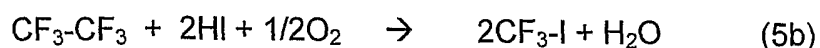
In yet another embodiment, W is hydrogen and Z is chlorine (4a), wherein the process proceeds, with or without O₂, at least in part according to the following equation:



In still another embodiment, W is CF₃ and Z is iodine (5a), wherein the process proceeds, with or without O₂, at least in part according to the following equation:



In still a further embodiment, W is CF₃ and Z is hydrogen (5b), wherein the process proceeds, with or without O₂, at least in part according to the following equation:

**Process Conditions:**

In the practice of the process of the present invention, the step of contacting is preferably carried out at a temperature from about 20 °C to about 650 °C, at a pressure from about 1 atm to about 100 atm, and for a length of time from about 0.01 sec to about 300 hours.

The process can be either a batch process or it can be a continuous process.

The reactor can further comprise a diluent, such as, a gas, a solvent or a mixture thereof. When the diluent is a gas, the diluent can be nitrogen, helium, argon or a mixture thereof. When the diluent is a solvent, the diluent is a solvent, which is preferably a liquid fluorocarbon.

The process can further include one or more of the following steps:

- (1) passing the trifluoromethyl iodide through a scrubber containing an aqueous alkali solution;
- (2) passing the trifluoromethyl iodide through a scrubber containing a drying agent;
- (3) cooling at a temperature below the boiling temperature of the trifluoromethyl iodide to condense; and
- (4) isolating the trifluoromethyl iodide from the reaction mixture in substantially pure form.

In operation, preferably at least 10 wt% of the reactants are converted to trifluoromethyl iodide. More preferably, at least 80 wt% of the reactants are converted to trifluoromethyl iodide, and most preferably, at least 95 wt% of the reactants are converted to trifluoromethyl iodide.

The following non-limiting examples are illustrative of the various embodiments of the present invention. It is within the ability of a person of ordinary skill in the art to select other variable from among the many known in the art without departing from the scope of the present invention. Accordingly, these examples shall serve to further illustrate the present invention, not to limit them.

Unless otherwise indicated, all parts and percentages are on a weight basis.

Example 1

One-step synthesis of CF₃I from CHF₃

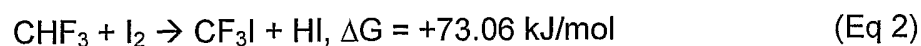
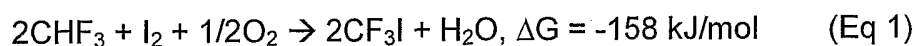
CF₃I is synthesized in a cost-effective way by reacting CHF₃ with I₂ and O₂ (or Air) in the presence of a catalyst including one or more iodide, nitrate, oxide, bromide, carbonate, chloride, acetate, acetylacetonate salts of Cu (II), Hg (II), Pt (II), Pd (II), Co (III), Mn (III), Rh (III), Ni (II), V (IV), Ti (III), and Ge (III) at 50-600°C in a vapor or liquid-phase process.

The catalyst salts can be used directly (100 wt%) or a portion (2-60 wt%) on an active support such as activated carbon, alumina, SiO₂, or ZrO₂.

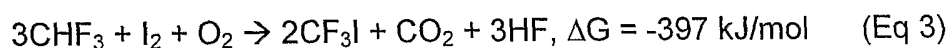
A mixture of salts supported on an active carbon, alumina, glass, SiO₂, SBA-15 support can also be used to obtain higher selectivity to CF₃I formation.

Thus, 20 SCCM (Standard Cubic Centimeter Per Minute) of CHF₃ is passed through a 50 cc 2wt%Cu-5wt%Pd-3wt%Pt/C catalyst bed placed in a 1/2-inch Monel reactor in the presence of 20 SCCM of air or O₂ and 20 SCCM of Iodine at 550°C to yield 40-95 mol% of CF₃I. The product mixture is analyzed by GC and GCMS.

Stoichiometric amount of O₂ is necessary for a thermodynamically favorable pathway (Eq 1) as written below because without the presence of O₂ the reaction is not favorable (Eq 2):



The reaction of CHF₃, I₂ and O₂ can also go in a different pathway as written below:



Eq 1 and 3 are both possible on the same active catalyst site, thus, the overall rate of CF₃I production will be the sum total of the rate of Eq 1 and Eq 3.

CHF₃, which is a common byproduct from fluorocarbon industries, can also be synthesized easily by vapor phase reaction of HF with CHCl₃ in the presence of a chromium oxide based catalyst at 200-450°C. Thus, the overall process is highly cost effective.

Example 2

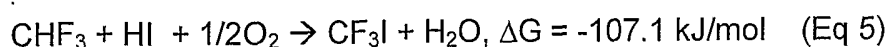
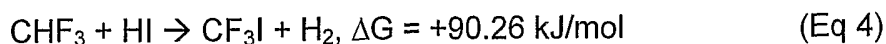
Preparation of CF₃I by Oxidative Iodination of CHF₃

CF₃I is synthesized in a cost-effective way by reacting CHF₃ with HI and O₂ (or Air) in the presence of a catalyst including one or more iodide, nitrate, oxide, bromide, carbonate, chloride, acetate, acetylacetonate salts of Mn (III), V (IV), Cr (III), Mo, Co (III), Ti (III), and Ge (III) at 50-600°C in a vapor phase process. The catalyst salts can be used directly (100 wt%) or a portion (2-60 wt%) on an active support such as activated carbon, alumina, SiO₂, and ZrO₂.

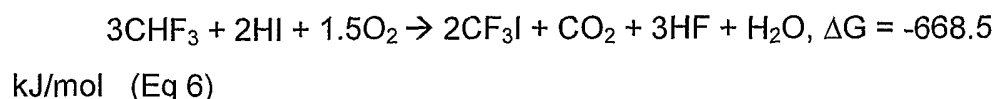
A mixture of salts can be used alone (100 wt%) or it can be supported on an active support to obtain higher selectivity to CF₃I formation.

Thus, 20 SCCM of CHF₃ and 20 SCCM of HI are passed through a 50 cc V₂O₅ or Pd-Pt/C catalyst bed placed in a 1-inch Monel reactor in the presence of 20 SCCM of air or O₂ and at 500°C to yield 67% of CF₃I. The product mixtures are analyzed by GC and GCMS.

Stoichiometric amount of O₂ is necessary for a thermodynamically favorable pathway (Eq 5) as written below because without the presence of O₂ the reaction is not favorable (Eq 4):



The reaction of CHF₃, HI and O₂ can also proceed in a more favorable pathway (Eq 6) as written below:



CHF₃, which is a common by-product from fluorocarbon industries, can also be synthesized easily by the vapor phase reaction of HF with CHCl₃ in the presence of a chromium oxide based catalyst at 200-450°C. Thus, the overall process is highly cost effective.

Example 3

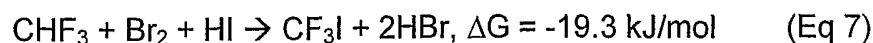
Catalytic one-step synthesis of CF₃I from CHF₃

CF₃I is synthesized in a cost-effective manner by reacting CHF₃ with Br₂ and HI in the presence of any one or a mixture of the following iodide, nitrate, oxide, bromide, carbonate, chloride, acetate, acetylacetonate salts, and preferably oxide salts, of Cu, Pt, Pd, Co, Mn, Rh, Ni, V, Ti, Th, Ge, and Cr, at 10-600°C in a vapor or liquid-phase process (Eq 1).

The catalyst salts can be used directly (100 wt%) or a portion (2-60 wt%) on an active support such as activated carbon, alumina, SiO₂, and ZrO₂.

A mixture of salts supported on an active support can also be used to obtain higher selectivity to CF₃I formation.

The reaction can be written as:



CHF_3 , which is a common byproduct from fluorocarbon industries, can also be synthesized easily by the vapor phase reaction of 3 moles of HF with one mole of CHCl_3 in the presence of a chromium oxide based catalyst at 200-450°C. Thus, the overall process is highly cost effective.

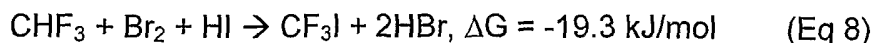
Thus, 20 SCCM of CHF_3 , 20 SCCM of Bromine and 30 SCCM of Iodine or HI were passed through a 50 cc Pd/C bed placed in a 1/2-inch Monel reactor to yield 70 mol% of CF_3I at 500°C. The reactor pressure was kept at 50 psig. The product mixtures exiting the reactor were analyzed by an on-line GC and GCMS couple.

Example 4

Catalytic one-step synthesis of CF_3I from CHF_3

CF_3I can be synthesized in a cost-effective way by reacting CHF_3 with Br_2 and HI in the presence of any one or a mixture of the iodide, nitrate, oxide, bromide, carbonate, chloride, acetate, acetylacetonate salts, and preferably oxide salts, of Cu, Pt, Pd, Co, Mn, Rh, Ni, V, Ti, Th, Ge, and Cr, at 10-600°C in a vapor or liquid-phase process (Eq 8). The catalyst salts can be used directly (100 wt%) or a portion (2-60 wt%) on an active support such as activated carbon, alumina, SiO_2 , and ZrO_2 . A mixture of salts supported on an active support can also be used to obtain higher selectivity to CF_3I .

The reaction can be written as:



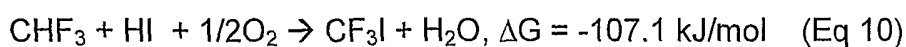
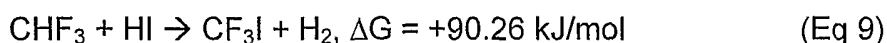
CHF_3 , which is a common byproduct from fluorocarbon industries, can also be synthesized easily by the vapor phase reaction of 3 moles of HF with one mole of CHCl_3 in the presence of a chromium oxide based catalyst at 200-450°C. Thus the overall process is highly cost effective.

Example 5

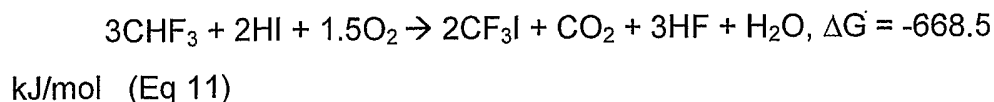
Oxidative Iodination of CHF_3 to CF_3I

CF_3I can be synthesized in a cost-effective way by reacting CHF_3 with HI and O_2 (or Air) in the presence of a catalyst including one or more iodide, nitrate, oxide, bromide, carbonate, chloride, acetate, acetylacetonate salts of Mn(III), V(IV), Cr(III), Mo, Co(III), Ti(III), and Ge(III), at 50-600°C in a vapor phase process. The catalyst salts can be used directly (100 wt%) or a portion (2-60 wt%) on an active support such as activated carbon, alumina, SiO_2 , and ZrO_2 . A mixture of salts can also be used alone (100 wt%) as well as supported on an active support to obtain higher selectivity to CF_3I formation.

Stoichiometric amount of O_2 is necessary for a thermodynamically favorable pathway (Eq 10) as written below because without the presence of O_2 the reaction is not favorable (Eq 9):



The reaction of CHF₃, HI and O₂ can also go in a more favorable pathway (Eq 11) as written below:



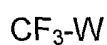
CHF₃, which is a common byproduct from fluorocarbon industries, can also be synthesized easily by the vapor phase reaction of HF with CHCl₃ in the presence of a chromium oxide based catalyst at 200-450°C. Thus the overall process is highly cost effective.

The present invention has been described with particular reference to the preferred embodiments. It should be understood that variations and modifications thereof can be devised by those skilled in the art without departing from the spirit and scope of the present invention. Accordingly, the present invention embraces all such alternatives, modifications and variations that fall within the scope of the appended claims.

DIRECT ONE-STEP SYNTHESIS OF CF₃-I**WHAT IS CLAIMED IS:**

1. A process for the preparation of trifluoromethyl iodide, comprising the step of:

contacting in a reactor a compound represented by the formula:



and a compound represented by the formula:



wherein W is selected from the group consisting of CF₃, hydrogen and bromine; Z is selected from the group consisting of hydrogen, iodine and chlorine; and wherein said step of contacting is carried out, optionally in the presence of a catalyst and further optionally in the presence of air, at a temperature, pressure and for a length of time sufficient to produce said trifluoromethyl iodide.

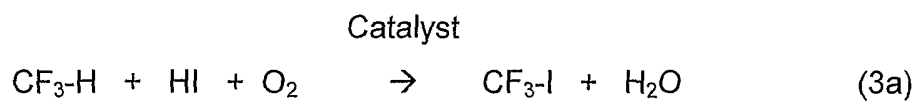
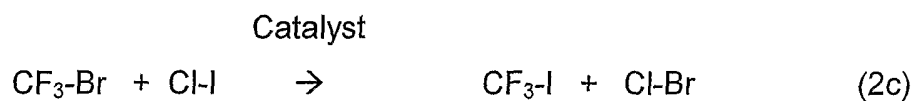
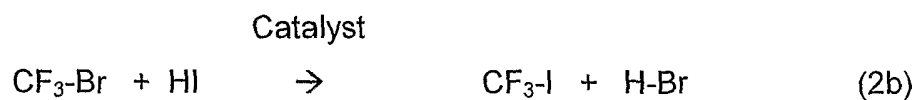
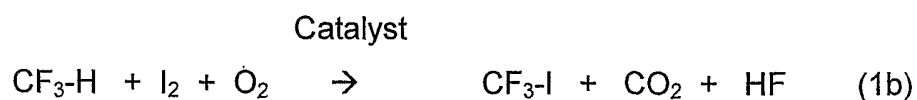
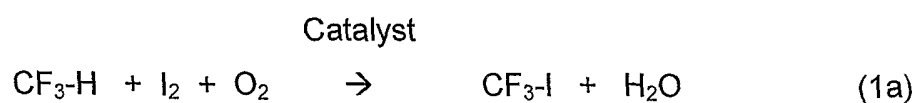
2. The process of claim 1, wherein W is hydrogen and Z is selected from the group consisting of iodine, hydrogen and chlorine.

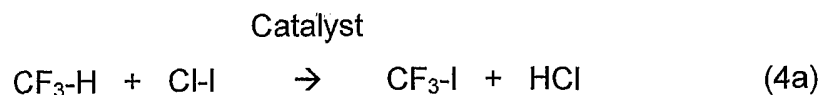
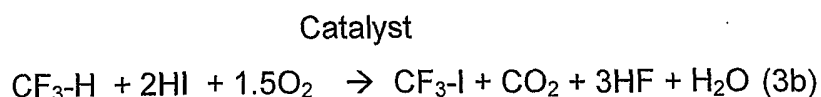
3. The process of claim 1, wherein W is bromine and Z is selected from the group consisting of iodine, hydrogen and chlorine.

4. The process of claim 1, wherein W is CF₃ and Z is selected from the group consisting of iodine and hydrogen.

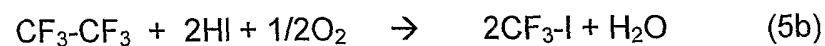
5. The process of claim 1, wherein said step of contacting is carried out at a temperature from about 20 °C to about 650 °C, at a pressure from about 1 atm to about 100 atm and for a length of time from about 0.01 sec to about 300 hours.

6. The process of claim 1, wherein the process proceeds at least in part according to the following equations:





or



7. The process of claim 1, wherein the process is a batch or a continuous process.

8. The process of claim 1, wherein the reactor further comprises a diluent selected from the group consisting of a liquid fluorocarbon solvent and a gas selected from the group consisting of: nitrogen, helium, argon and a mixture thereof.

9. The process of claim 1, further comprising the step of:

passing the trifluoromethyl iodide through a scrubber containing a drying agent or an aqueous alkali solution.

10. The process of claim 1, wherein at least 10 wt% of the reactants are converted to trifluoromethyl iodide.