DIRECT ONE-STEP SYNTHESIS FROM CF3-I
DIREKTE EINSTUFEN-SYNTHESE VON CF3-I
SYNTHESE DIRECTE EN UNE ETAPE A PARTIR DE CF3-I

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Proprietor: Honeywell International Inc. Morristown, NJ 07960 (US)
Inventors:
• MUKHOPADHYAY, Sudip Buffalo, NY 14210 (US)
• HSUEHSUNG, Tung Getzville, NY 14068 (US)
Representative: Hucker, Charlotte Jane Kilburn & Strode LLP 20 Red Lion Street London WC1R 4PJ (GB)

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BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

[0001] 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-H and H-I.

2. DESCRIPTION OF THE PRIOR ART

[0002] 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 CF₃-I 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 proceeds via CF₂ carbenes formed on the catalyst surface as intermediates, followed by carbene disproportionation to CF₃ radicals, followed by reaction with I₂ to give CF₃-I (see Nagasaki, Noritaka et al., Catalysis Today (2004), 88(3-4), 121-126).


[0004] DE 1805457 (1970) describes the preparation of CF₃-I and C₂F₅-I from the reaction of corresponding bromides and I₂ without solvent.


[0010] 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 CF₃-I.

[0011] Furthermore, there is no report in the literature of any catalytic vapor-phase process for making CF₃-I 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.

[0012] The above described problems can be avoided by the use of a process for the preparation of trifluoromethyl iodide from CF₃-H and H-I.

SUMMARY OF THE INVENTION

[0013] 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:

CF₃-H

and a compound represented by the formula:

H-I

[0014] 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.

[0015] 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.

[0016] These and other benefits of the present process will become more evident from the detailed description of the
The present invention provides a process for the preparation of trifluoromethyl iodide from CF₃-H and H-I.

CF₃I is a non-toxic, non-flammable, low global warming potential compound with almost zero ozone depletion potential (See, for example, Dhooge 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 CF₃I 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, CHF₃ and Hydrogen Iodide as the starting materials to produce CF₃I 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 CF₃I.

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

Preferred Embodiments:

In a preferred embodiment, (3a or 3b), the process proceeds at least in part according to the following equation:

\[
\text{Catalyst} \\
\text{CF}_3\text{H} + \text{HI} + \text{O}_2 \rightarrow \text{CF}_3\text{I} + \text{H}_2\text{O} \quad (3a)
\]

or according to the following equation:

\[
\text{Catalyst} \\
\text{CF}_3\text{H} + 2\text{HI} + 1.5\text{O}_2 \rightarrow \text{CF}_3\text{I} + \text{CO}_2 + 3\text{HF} + \text{H}_2\text{O} \quad (3b)
\]

Process Conditions:

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

Example 1 (Not according to the invention)

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):

2CHF₃ + I₂ + 1/2O₂ → 2CF₃I + H₂O, ΔG = -158 kJ/mol (Eq 1)

CHF₃ + I₂ → CF₃I + HI, ΔG = +73.06 kJ/mol (Eq 2)

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

3CHF₃ + I₂ + O₂ → 2CF₃I + CO₂ + 3HF, ΔG = -397 kJ/mol (Eq 3)

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 mixture is 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):

CHF₃ + HI → CF₃I + H₂, ΔG = +90.26 kJ/mol (Eq 4)

CHF₃ + HI + 1/2O₂ → CF₃I + H₂O, ΔG = -107.1 kJ/mol (Eq 5)
The reaction of CHF₃, HI and O₂ can also proceed in a more favorable pathway (Eq 6) as written below:

\[
3\text{CHF}_3 + 2\text{HI} + 1.5\text{O}_2 \rightarrow 2\text{CF}_3\text{I} + \text{CO}_2 + 3\text{HF} + \text{H}_2\text{O}, \Delta G = -668.5 \text{ kJ/mol} \quad (\text{Eq } 6)
\]

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:

\[
\text{CHF}_3 + \text{Br}_2 + \text{HI} \rightarrow \text{CF}_3\text{I} + 2\text{HBr}, \Delta G = -19.3 \text{ kJ/mol} \quad (\text{Eq } 7)
\]

CHF₃, 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 CHCl₃ 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 CHF₃, 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 CF₃I 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 CF₃I from CHF₃**

CF₃I can be synthesized in a cost-effective way by reacting CHF₃ with Br₂ 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, SiO₂, and ZrO₂. A mixture of salts supported on an active support can also be used to obtain higher selectivity to CF₃I.

The reaction can be written as:

\[
\text{CHF}_3 + \text{Br}_2 + \text{HI} \rightarrow \text{CF}_3\text{I} + 2\text{HBr}, \Delta G = -19.3 \text{ kJ/mol} \quad (\text{Eq } 8)
\]

CHF₃, 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 CHCl₃ 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 CHF₃ to CF₃I**

CF₃I can be 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 also be used alone (100 wt%) as well as supported on an active support to obtain higher selectivity.
[0055] Stoichiometric amount of O₂ is necessary for a thermodynamically favorable pathway (Eq 10) as written below because without the presence of O₂ the reaction is not favorable (Eq 9):

\[
\text{CHF}_3 + \text{HI} \rightarrow \text{CF}_3\text{I} + \text{H}_2, \Delta G = +90.26 \text{ kJ/mol (Eq 9)}
\]

\[
\text{CHF}_3 + \text{HI} + \frac{1}{2}\text{O}_2 \rightarrow \text{CF}_3\text{I} + \text{H}_2\text{O}, \Delta G = -107.1 \text{ kJ/mol (Eq 10)}
\]

[0056] The reaction of CHF₃, HI and O₂ can also go in a more favorable pathway (Eq 11) as written below:

\[
3\text{CHF}_3 + 2\text{HI} + 1.5\text{O}_2 \rightarrow 2\text{CF}_3\text{I} + \text{CO}_2 + 3\text{HF} + \text{H}_2\text{O}, \Delta G = -668.5 \text{ kJ/mol (Eq 11)}
\]

[0057] CHF₃, which 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.

Claims

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

   contacting in a reactor a compound represented by the formula:

   \[ \text{CF}_3\text{-H} \]

   and a compound represented by the formula:

   \[ \text{H-I} \]

   ; and wherein said step of contacting is carried out at a temperature, pressure and for a length of time sufficient to produce said trifluoromethyl iodide.

2. The process of claim 1, wherein said step of contacting is carried out at a temperature from 20 °C to 650 °C, at a pressure from 0.1×10⁶ Pa (1 atm) to 10⁵ Pa (100 atm) and for a length of time from 0.01 sec to 300 hours.

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

   \[
   \text{Catalyst} \quad \text{CF}_3\text{-H} + \text{HI} + \text{O}_2 \quad \rightarrow \quad \text{CF}_3\text{I} + \text{H}_2\text{O} \quad (3a)
   \]

   \[
   \text{Catalyst} \quad \text{CF}_3\text{-H} + 2\text{HI} + 1.5\text{O}_2 \rightarrow \text{CF}_3\text{I} + \text{CO}_2 + 3\text{HF} + \text{H}_2\text{O} \quad (3b)
   \]

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

5. 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.
6. 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.

Patentansprüche

1. Verfahren zur Herstellung von Trifluormethyljodid, bei dem man:

   in einem Reaktor eine Verbindung der Formel:

   \[
   \text{CF}_3\text{H}
   \]

   und eine Verbindung der Formel:

   \[
   \text{H-I}
   \]

in Berührung bringt, wobei man das Inberührungbringen bei einer Temperatur, bei einem Druck und über einen Zeitraum, die bzw. der zur Bildung des Trifluormethyljodids ausreicht, durchführt.

2. Verfahren nach Anspruch 1, bei dem man das Inberührungbringen bei einer Temperatur von 20°C bis 650°C, bei einem Druck von 0,1.10^6 Pa (1 atm) bis 10^8 Pa (100 atm) und über einen Zeitraum von 0,01 s bis 300 Stunden durchführt.

3. Verfahren nach Anspruch 1, bei dem das Verfahren zumindest zum Teil gemäß den folgenden Gleichungen abläuft:

   \[
   \text{Katalysator} \\
   \text{CF}_3\text{-H} + \text{HI} + \text{O}_2 \rightarrow \text{CF}_3\text{-I} + \text{H}_2\text{O} \quad (3a)
   \]

   \[
   \text{Katalysator} \\
   \text{CF}_3\text{-H} + 2\text{HI} + 1,5\text{O}_2 \rightarrow \text{CF}_3\text{-I} + \text{CO}_2 + 3\text{HF} + \text{H}_2\text{O} \quad (3b)
   \]

4. Verfahren nach Anspruch 1, bei dem es sich um ein diskontinuierliches oder kontinuierliches Verfahren handelt.


6. Verfahren nach Anspruch 1, bei dem man ferner:

   das Trifluormethyljodid durch einen ein Trocknungsmittel oder eine wässrige Alkalilösung enthaltenden Wäschereit.

Revendications

1. Procédé de préparation d’iodure de trifluorométhyle, comprenant l’étape de :

   mise en contact dans un réacteur d’un composé représenté par la formule :
et d'un composé représenté par la formule :

\[ \text{CF}_3\text{-H} \]

et dans lequel ladite étape de mise en contact est réalisée à une température, sous une pression et pendant une durée suffisantes pour produire ledit iodure de trifluorométhyle.

2. Procédé selon la revendication 1, dans lequel ladite étape de mise en contact est réalisée à une température de 20°C à 650°C, sous une pression de 0,1.10^6 Pa (1 atm) à 10^5 Pa (100 atm) et pendant une durée de 0,01 s à 300 heures.

3. Procédé selon la revendication 1, dans lequel le procédé se déroule au moins en partie selon les équations suivantes :

\[ \text{Catalyseur} \]

\[ \text{CF}_3\text{-H} + \text{HI} + \text{O}_2 \rightarrow \text{CF}_3\text{-I} + \text{H}_2\text{O} \quad (3a) \]

\[ \text{Catalyseur} \]

\[ \text{CF}_3\text{-H} + 2\text{HI} + 1,5\text{O}_2 \rightarrow \text{CF}_3\text{-I} + \text{CO}_2 + 3\text{HF} + \text{H}_2\text{O} \quad (3b) \]

4. Procédé selon la revendication 1, dans lequel le procédé est un procédé discontinu ou continu.

5. Procédé selon la revendication 1, dans lequel le réacteur comprend en outre un diluant choisi dans le groupe constitué par un solvant fluorocarbure liquide et un gaz choisi dans le groupe constitué par : l’azote, l’hélium, l’argon et un mélange de ceux-ci.

6. Procédé selon la revendication 1, comprenant en outre l’étape consistant à :

faire passer l’iodure de trifluorométhyle à travers un purificateur contenant un agent siccatif ou une solution aqueuse d’alcali.
REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- DE 1805457 [0004]
- EP 266281 A1 [0006]

Non-patent literature cited in the description