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(54) Preparation of high purity fluorinated peroxides

(57) High-purity fluorinated peroxides are prepared in a simplified process in which carbonyl fluoride is reacted with a hypofluorite to produce a gaseous reaction product which is essentially free of unreacted hypofluorite; unreacted carbonyl fluoride and by productsare removed from the gaseous reaction product under gas phase conditions; and then the fluorinated peroxideis collected in gas phase.

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Description

BACKGROUND OF THE INVENTION

[0001] Fluorinated peroxides are powerful oxidizing agents and have value as free radical generators and etchants in the manufacture of electronic components. Perfluorodimethyl peroxide or sometimes called bis(trifluoromethyl)peroxide is an example of a common fluoroperoxide employed in these applications.

[0002] One of the many requirements imposed by the electronic industry is that of high purity. The resulting product must be substantially free of unreacted contaminants. Because of the highly reactive and hazardous nature of the reactants and byproducts formed in the synthesis, there are many safety issues and extreme care is required in synthesis and recovery of high purity product.

[0003] The following articles and patents are representative of the art with respect to fluorinated peroxides including the production of perfluorodimethyl peroxide and their recovery.

[0004] USP 3,100,803 and USP 3,230,264 (CIP of '264) disclose the synthesis of perfluorodimethyl peroxide by the reaction of equal molar amounts of carbonyl fluoride with trifluoromethyl hypofluorite in the presence of a metal fluoride catalyst. Reaction temperatures generally are in excess of 200 °C. Samples of products are collected by condensing in traps cooled by liquid oxygen. The condensate then is separated by distillation. In other procedures, carbon monoxide is reacted with fluorine in various ratios, thus generating carbonyl fluoride and trifluoromethyl hypofluorite *in situ.*

[0005] USP 3,202,718 discloses a method for the preparation of bis (trifluoromethyl) peroxide (BTMP) by reacting carbonyl fluoride (COF_2) with chlorine trifluoride (ClF_3) at temperatures ranging from 0 to 300 °C, preferably between 100 and 250 °C, in the presence of fluoride salts. Isolation and purification of BTMP is effected by passing the reaction product through a tube of granulated calcium chloride, scrubbing with water and dilute caustic to remove residual chlorine, hydrogen fluoride, and carbonyl fluoride, passing the scrubbed stream through a -80 °C trap to freeze out water and condense the bis(trifluoromethyl)peroxide, and then passing the liquid stream through a liquid nitrogen trap to prevent loss of bis(trifluoromethyl) peroxide. When tetrafluoromethane is present as a byproduct, it is removed as a last step by distillation.

[0006] Roberts, H.L., Preparation of Bis(trifluoromethyl) Peroxide and its Reduction with Hexafluoropropene, J. Chem. Soc. (1964) 4538 discloses a process for the preparation of BTMP through the reaction of COF_2 with CF_3OF (molar ratio of 1.47:1) at high-temperature and high-pressure (275 °C and 780 psig/37.3 kPa) in a nickel autoclave. The autoclave is cooled to room temperature and the products remaining in the autoclave are removed and the gases passed through liquid air traps. Then the condensate is distilled in a Podbielniak column. The recovered product then is reacted with hexafluoropropene and a product consisting of telomers $CF_3O]C_3F_6]_n$-OCF_3 where n ≥2 is formed.

[0007] Gard, G. L., et al, Reactions of Xenon with Certain Strong Oxidizing Agents, The University of Chicago Press, Chicago, 1963 (p 109-111 disclose various reactions of xenon with various oxidizing agents. In one example xenon is reacted with trifluoromethyl hypofluorite to produce xenon difluoride and BTMP. In the recovery step, the reaction product at 225 °C is cooled in a water bath, then cooled to -78 °C and the volatile product pumped away and through a liquid nitrogen trap. The volatile materials other than xenon are shown to be CF_3OF, and CF_3OOCF_3 and the material remaining in the tube is xenon difluoride.

[0008] US 4,499,024 discloses a process for the production of bisfluoroxydifluoromethane (BDM) by the reaction of carbon dioxide and fluorine in the presence of a cesium fluoride catalyst, The principal impurities are CF_3OF, CO_2, and CF_4 although trace amounts of CF_3OOCF_3 can be present. Separation to produce high purity product is accomplished by liquefaction and venting the gaseous impurities.

[0009] US 4,654,444 discloses a process for producing fluorine containing diacylperoxides by the reaction of an acyl halide, e.g., α,α-difluoro-β-*t*-butoxypropionyl chloride with sodium peroxide in water and extracting the product with a suitable solvent.

BRIEF SUMMARY OF THE INVENTION

[0010] This invention is directed to an improvement in a process for producing high-purity fluorinated peroxides typically formed by the reaction of a carbonyl fluoride with a hypofluorite. The improvement resides in a simplified process for the synthesis and gas phase recovery of high purity fluorinated peroxide product and comprises the steps:

(a) reacting the carbonyl fluoride with the hypofluorite under conditions such that a gaseous reaction product comprised of the fluorinated peroxide and unreacted carbonyl fluoride which is essentially free of unreacted hypofluorite is formed;

(b) removing unreacted carbonyl fluoride and any byproducts from the gaseous reaction product under gas phase conditions thereby generating a gaseous product stream containing the fluorinated peroxide; and then,

(c) collecting the fluorinated peroxide from step (b) in gas phase.

[0011] Significant advantages can be achieved using the simplified gas phase recovery process and some of these include:

an ability to produce fluorinated peroxides of sufficiently high purity to be used directly for electronics applications;

an ability to eliminate the low temperature condensation steps and distillation steps associated with prior purification processes;

an ability to produce such high purity fluorinated peroxide without the need for a distillation step; and,

an ability to reduce the hazards associated with low temperature recovery processes employing condensation in producing high purity fluorinated peroxides;

DETAILED DESCRIPTION OF THE INVENTION

[0012] This invention is directed to an improvement in a process for the production of high purity fluorinated peroxides formed by reacting a carbonyl fluoride with a hypofluorite. The process is generally comprised of two steps, the first step involving the synthesis of the fluorinated peroxide containing reaction product and the second step involving the gas phase recovery of the fluorinated peroxide from the reaction product.

[0013] The first step in the process is comprised of reacting a carbonyl fluoride with a hypofluorite such as trifluoromethyl hypofluorite to form the fluorinated peroxide. The hypofluorite may be prepared prior to contact with the carbonyl fluoride or formed, *in situ,* as for example by the reaction of carbon monoxide with fluorine in the presence of a catalyst, e.g. a fluoride salt. Likewise the carbonyl fluoride can be formed prior to reaction with the hypofluorite or *in situ* as for example by reacting carbon monoxide with fluorine. Depending upon the reaction scheme selected reactants may be preformed or formed *in situ* as one desires.

[0014] Examples of hypofluorites suited for reaction include the C_{1-8} alkylhypofluorites and C_{1-8} bisalkylhypofluorites such as trifluoromethyl hypofluorite, chlorodifluoromethyl hypofluorite, pentafluoroethyl hypofluorite, heptafluoropropyl hypofluorite, and bis(fluoroxy)difluoromethane.

[0015] Preferred routes to desired fluorinated peroxides are described by the equations:

A

$$\text{excess } COF_2 + R_fOF \xrightarrow{\Delta} R_fOOCF_3 + COF_2 \qquad R_f = C_xF_{2x+1}\ (x = 1\text{-}8)$$

`B

$$\text{excess } COF_2 + R'_f(OF)_2 \longrightarrow R'_f(OOCF_3)_2 + COF_2 \qquad R'_f = C_xF_{2x}\ (x = 1\text{-}8)$$

[0016] It has been found that one can reduce the hazards associated with the recovery of fluorinated peroxides including the simplification of the recovery process by initially controlling the reaction conditions associated with the synthesis. An initial objective in the synthesis of the fluorinated peroxide is one of effecting essentially complete conversion of the hypofluorite employed in the reaction. Reaction conditions are controlled to drive the equilibrium based reaction to completion leaving essentially no hypofluorite in the reaction product. It is preferred that the reaction product have less than 0.5% hypofluorite generally less than 0.1 % and preferably less than 0.05% by weight.

[0017] In a preferred embodiment, bis(trifluoromethyl) peroxide is produced by a process which comprises:

(a) reacting carbonyl fluoride with trifluoromethyl hypofluorite under conditions such that a gaseous reaction product comprised of bis(trifluoromethyl) peroxide, unreacted carbonyl fluoride and byproducts and having less than 0.5% trifluoromethyl hypofluorite is formed;

(b) removing unreacted carbonyl fluoride and by products from the gaseous reaction product under gas phase conditions thereby generating a gaseous product stream containing said bis(trifluoromethyl) peroxide; and then,

(c) collecting the bis(trifluoromethyl) peroxide from step (b) in gas phase.

[0018] A key factor leading to a reaction product essentially free of unreacted hypofluorite lies in the reaction stoichiometry. A stoichiometric excess of carbonyl fluoride to the hypofluorite is employed to drive the reaction as represented by the above equations to completion. Molar ratios of carbonyl fluoride to hypofluorite are generally from 1.1 to 3:1 and preferably from 1.2 to 1.7:1. Other byproducts commonly formed in the reaction in small to trace amount include carbon dioxide, hydrogen fluoride, fluorine, and adventitious water. Temperatures of from 150 to 350 °C and autogeneous pressures are typical. Reaction conditions vary depending on the hypofluorite used and the fluorinated peroxide being made.

[0019] It has been found that by conducting the reaction of carbonyl fluoride with the hypofluorite under conditions such that essentially no unreacted hypofluorite remains, one can implement a gas phase recovery process to achieve removal of the unreacted carbonyl fluoride and byproducts from the reaction product and recover the fluorinated peroxide without passing the reaction product through low temperature condensation traps. By maintaining gas phase conditions throughout recovery one avoids the hazards associated with highly reactive compounds in condensed form.

[0020] In the broadest sense recovery of the fluorinated peroxide from the gaseous reaction product can be achieved by passing the gaseous reaction product through a sorbent bed capable of removing the contaminating carbonyl fluoride, and any byproducts. Alkali exchanged 3 to 5 A zeolites and anhydrous soda-lime granules are exemplary of the adsorbents capable of removing such contaminants.

[0021] In the preferred recovery process the gaseous reaction product is initially scrubbed with an aqueous medium, typically an aqueous alkaline medium, in order to hydrolyze unreacted carbonyl fluoride, and neutralize any acidic compounds present in the gas stream. An alkaline solution having from 5 to 50% by weight of alkali, e.g., sodium hydroxide, potassium hydroxide, calcium hydroxide and so forth is a preferred scrubbing agent.

[0022] In the second part of the recovery process, the thus aqueous treated reaction product is passed through one or more absorptive beds to assist in the removal of unreacted carbonyl fluoride and byproduct carbon oxides, e.g., CO_2, and entrained H_2O. Representative adsorbents suited for removing contaminants from the fluorinated peroxide product include zeolites such as 3 and 4 A zeolites and soda-lime. Small pore zeolites should be used so as to avoid reaction with the fluorinated peroxide product. In the event that some carbon oxides remain after passage through the adsorbent bed, the product may be passed through a reactant such as soda-lime which is capable of reacting with the carbon oxides or another bed of adsorbent.

[0023] The following examples are provided to illustrate various embodiments of the invention and are not intended to restrict the scope thereof.

Example 1

Preparation of Bis(trifluoromethyl)peroxide Mole Ratio 1.52:1

[0024] Reactants carbonyl fluoride, COF_2, and fluoroxytrifluoromethane, CF_3OF, were prepared in a flow system and collected in a clean and dry 600-cc Monel pressure reactor. A total of 500 mmol COF_2 and 328 mmol CF_3OF was collected representing a molar ratio of COF_2:CF_3OF of 1.52:1. The mixture of COF_2 and CF_3OF was heated under autogenous pressure to 274 °C over the course of 3.5 hours and then held at 274 °C for an additional 2 hours. After the specified time, the mixture was allowed to cool to ambient temperature. An infrared spectrum of the reactor contents indicated a mixture of COF_2 and bis(trifluoromethyl)peroxide (BTMP), CF_3OOCF_3, with no CF_3OF observed.

[0025] The gaseous contents of the reactor were passed through a purification train consisting of a column of H_2O followed by a bed of heat-activated 4Å molecular sieve and subsequently collected in a clean and dry collection cylinder at sub-ambient temperature. Infrared analysis of the product in the collection cylinder indicated high-purity CF_3OOCF_3 (BTMP) with no evidence of any CO_2, H_2O, COF_2, or CF_3OF present. The BTMP product weighed 33.3 g which represents a yield of 60%.

[0026] Using this reaction and recovery protocol one is able to avoid the hazards associated with the presence of CF_3OF in the reaction product and the separation hazards associated therewith.

Example 2

Preparation of Bis(trifluoromethyl)peroxide Mole Ratio of 1.25:1

[0027] In an experiment similar to that described in Example 1, 443 mmol of COF_2 and 354 mmol CF_3OF was collected representing a molar ratio of COF_2:CF_3OF of 1.25:1. The mixture of COF_2 and CF_3OF was heated under autogenous pressure to > 270 °C and then held between 270 °C and 280 °C for 3.5 hours. After the specified time, the mixture was allowed to cool to ambient temperature. An infrared spectrum of the reactor contents indicated a mixture of COF_2 and bis(trifluoromethyl)peroxide (BTMP), CF_3OOCF_3, with no CF_3OF observed.

[0028] The product of the reaction was purified and collected according to the method described in Example 1. Infrared analysis of the product in the collection cylinder indicated high-purity CF_3OOCF_3 (BTMP) with no evidence of any CO_2, H_2O, COF_2, or CF_3OF. The BTMP product weighed 36.9 g which represents a yield of 61%.

Example 3

Preparation of Bis(trifluoromethyl)peroxide Mole Ratio 1.99:1

[0029] Reactants carbonyl fluoride, COF_2, and fluoroxytrifluoromethane, CF_3OF, were distilled into a clean and dry 600-cc Monel pressure reactor. A total of 558 mmol COF_2 and 281 mmol CF_3OF was used representing a molar ratio of COF_2:CF_3OF of 1.99:1. The mixture of COF_2 and CF_3OF was heated under autogenous pressure to 275 °C over the course of 5.5 hours and then held at > 269 °C for an additional hour. After the specified time, the mixture was allowed to cool to ambient temperature. An infrared spectrum of the reactor contents indicated a mixture of CO_2, COF_2 and bis (trifluoromethyl)peroxide (BTMP), CF_3OOCF_3, with no CF_3OF observed.

[0030] The contents of the reactor were passed through a purification train consisting of a column of H_2O followed by a bed of heat-activated 4Å molecular sieves and the treated contents subsequently collected in a clean and dry collection cylinder at sub-ambient temperature. Infrared analysis of the product in the collection cylinder indicated a mixture of CF_3OOCF_3 (BTMP) and CO_2. Apparently the molecular sieves were not completely effective at removing CO_2. The contents of the collection cylinder were then passed through a column of soda-lime and collected in a clean dry cylinder. Analysis of the cylinder contents indicated high-purity CF_3OOCF_3 (BTMP) with no evidence of any CO_2, H_2O, COF_2, or CF_3OF.

[0031] This example shows that increasing the molar ratio of carbonyl fluoride to trifluoromethyl hypofluorite above 1.7, although effective for minimizing the level of trifluoromethyl hypofluorite in the reaction product, results in increased carbon oxide content, as well as increasing the level of unreacted carbonyl fluoride, and that increased load may place unnecessary burdens on the scrubbing and adsorbent systems in addition to the loss of reactant carbonyl fluoride.

Example 4

Purification of Crude Bis(trifluoromethyl)peroxide With Soda-Lime

[0032] A crude sample containing a mixture of BTMP and COF_2 was passed through a column of soda-lime and then collected in a clean and dry collection cylinder. Analysis of the cylinder contents indicated high-purity CF_3OOCF_3 (BTMP) with no evidence of any CO_2, H_2O, COF_2, or CF_3OF.

[0033] This example demonstrates that it is possible to employ a single adsorbent to remove substantially all of the contaminates from a reaction product containing the fluorinated peroxide.

Example 5

Purification of Crude Bis(trifluoromethyl)peroxide With Water and Soda-Lime

[0034] A crude sample containing a mixture of BTMP and COF_2 was passed through a column of H_2O and subsequently through a column of soda-lime and then collected in a clean and dry collection cylinder. Analysis of the cylinder contents indicated high-purity CF_3OOCF_3 (BTMP) with no evidence of any CO_2, H_2O, COF_2, or CF_3OF.

Comparative Example 6

Purification of Crude Bis(trifluoromethyl)peroxide With Soda-Lime

[0035] An attempt to purify a crude sample containing a mixture of BTMP and CF_3OF by passing the mixture through a column of soda-lime was not successful as the process generated oxygen as well as a tremendous amount of localized heat. That heat caused the subsequent decomposition of the remaining BTMP.

[0036] This example shows the unsuitability of the gas phase recovery of fluorinated peroxide product from a gaseous reaction product containing unreacted hypofluorite as is the case when COF_2 and CF_3OF are reacted in equal molar amounts. The scrubbing of the reaction product by contact with a column of water and removal of carbon oxides.

Claims

1. A process for producing a high-purity fluorinated peroxide by reacting a carbonyl fluoride with a hypofluorite which comprises the steps:

   (a) reacting said carbonyl fluoride with said hypofluorite under conditions such that a gaseous reaction product comprised of said fluorinated peroxide and unreacted carbonyl fluoride which is essentially free of unreacted hypofluorite is formed;
   (b) removing unreacted carbonyl fluoride from the gaseous reaction product under gas phase conditions thereby generating a gaseous product stream containing said fluorinated peroxide; and then,
   (c) collecting the fluorinated peroxide from step (b) in gas phase.

2. A process of Claim 1 wherein the reaction synthesis described in step (a) is represented by the formulas A and B:

   A

$$\text{excess } COF_2 + R_fOF \xrightarrow{\Delta} R_fOOCF_3 + COF_2 \qquad R_f = C_xF_{2x+1}\ (x = 1\text{-}8)$$

   B

$$\text{excess } COF_2 + R'_f(OF)_2 \longrightarrow R'_f(OOCF_3)_2 + COF_2 \qquad R'_f = C_xF_{2x}\ (x = 1\text{-}8)$$

3. A process of Claim 1 or 2 wherein the mole ratio of carbonyl fluoride to hypofluorite is from 1.1 to 3:1.

4. A process of Claim 3 wherein said mole ratio is from 1.2 to 1.7:1.

5. A process of any one of the preceding claims wherein the gaseous reaction product is initially contacted with an aqueous medium under conditions for hydrolyzing unreacted carbonyl fluoride.

6. A process of Claim 5 wherein the gaseous reaction product is contacted with the aqueous medium under conditions for hydrolyzing carbonyl fluoride and forming an acidic compound.

7. A process of any one of the preceding claims wherein the gaseous reaction product stream, after the optional aqueous treatment, is passed through an absorbent to remove any unreacted carbonyl fluoride, byproducts and water.

8. A process of Claim 7 wherein the adsorbent is a zeolite molecular sieve.

9. A process of Claim 8 wherein the molecular sieve is a 3A or 4A molecular sieve.

10. A process of Claim 7 wherein the adsorbent is a molecular sieve or soda-lime.

11. A process of any one of the preceding claims wherein the hypofluorite is selected from C_{1-8} alkylhypofluorites and C_{1-8} bisalkylhypofluorites.

12. A process of Claim 11 wherein the hypofluorite is selected trifluoromethyl hypofluorite, chlorodifluoromethyl hypofluorite, pentafluoroethyl hypofluorite, heptafluoropropyl hypofluorite, and bis(fluoroxy)difluoromethane.

13. A process of Claim 12 wherein the hypofluorite is trifluoromethyl hypofluorite.

14. A process of any one of the preceding claims wherein unreacted trifluoromethyl hypofluorite in the reaction product is present in an amount of less than 0.5% by weight.

15. A process of Claim 14 wherein unreacted trifluoromethyl hypofluorite in the reaction product is present in an amount of less than 0.1 % by weight.

16. A process of Claim 15 wherein unreacted trifluoromethyl hypofluorite in the reaction product is present in an amount of less 0.05% by weight.

17. A process of any one of the preceding claims wherein the carbonyl fluoride and trifluoromethyl hypofluorite are preformed prior to reaction.

18. A process of one of Claims 1 to 16 wherein the carbonyl fluoride and/or the trifluoromethyl hypofluorite are formed *in situ.*

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 06 25 4363

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A,D	US 320 264 A (PORTER, ROGER S ET AL) 18 August 1966 (1966-08-18) * the whole document *	1-18	INV. C07C409/16 C07C407/00
X	equations 2 and 3 * examples 1-3 * * table 1 * * column 4, lines 1-5 *	1-4	
Y	* examples 1-3 *	5-10	
A,D	US 3 202 718 A (ELLINGBOE ELLSWORTH K ET AL) 24 August 1965 (1965-08-24) * the whole document *	1-18	
Y	* example II *	5-10	
Y	US 5 622 682 A (TOM GLENN M [US]) 22 April 1997 (1997-04-22) summary of the invention * column 5, line 52 - line 55 *	8-10	
Y	DATABASE INTERNET University of Minnesota; 1 November 2004 (2004-11-01), STEVEN CLAAS: "Soda-Lime Vapor Trap" XP002408077 http://www.soils.umn.edu/research_old/hgl/Soda_Lime.html * abstract *	10	

			TECHNICAL FIELDS SEARCHED (IPC)
			C07C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	30 November 2006	Panday, Narendra

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 06 25 4363

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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30-11-2006

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 320264	A		NONE	
US 3202718	A	24-08-1965	NONE	
US 5622682	A	22-04-1997	NONE	

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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- US 4499024 A **[0008]**
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- **GARD, G. L. et al.** Reactions of Xenon with Certain Strong Oxidizing Agents. The University of Chicago Press, 1963, 109-111 **[0007]**