

DESCRIPTION

METHOD FOR PRODUCING BIS(HALOSULFONYL)AMINE

TECHNICAL FIELD

[0001]

5 The present invention relates to a method for producing bis(halosulfonyl)amine. More particularly, the present invention relates to an industrially advantageous method for producing bis(halosulfonyl)amine that makes it possible to inhibit the rapid generation of gas and reduce the amount of
10 halogenating agent used by controlling the reaction rate among sulfamic acid, the halogenating agent and a halosulfonic acid to nearly a constant rate from the initial stage to the final stage of the reaction.

 The present application claims priority on the basis of
15 Japanese Patent Application No. 2012-174209, filed in Japan on August 6, 2012, the contents of which are incorporated herein by reference.

BACKGROUND ART

[0002]

20 Salts of bis(fluorosulfonyl)amine are compounds that are useful in various fields such as in battery electrolytes, battery electrolyte additives or materials of electrically conductive coated films (Patent Document 1, Patent Document 2, Patent Document 3). In addition, bis(chlorosulfonyl)amine, by
25 reacting with a fluorinating agent or by carrying out a cation

exchange reaction after reacting with a fluorinating agent, can be derived to various salts of bis(fluorosulfonyl)amine, thereby making this a useful compound as well (Patent Document 4, Patent Document 5, Non-Patent Document 1).

5 [0003]

A known method for synthesizing bis(chlorosulfonyl)amine consists of mixing sulfamic acid, thionyl chloride and chlorosulfonic acid followed by heating the mixture and allowing to react (Patent Document 3, Patent Document 4, Patent Document 6, Non-Patent Document 2, Non-Patent Document 3).

Prior Art Documents

Patent Documents

[0004]

Patent Document 1: Japanese Unexamined Patent Application Publication (Translation of PCT Application) No. H08-511274

Patent Document 2: Japanese Patent Application, First Publication No. 2010-121114

Patent Document 3: Japanese Patent Application, First Publication No. 2010-168249

20 Patent Document 4: Japanese Patent Application, First Publication No. 2010-189372

Patent Document 5: Japanese Patent Application Publication (Translation of PCT Application) No. 2004-522681

Patent Document 6: Japanese Patent Application, First Publication No. H08-217745

Non-Patent Documents

[0005]

Non-Patent Document 1: Inorg. Synth., 11, 138-140 (1968)

Non-Patent Document 2: Eur. J. Org. Chem., 5165-5170 (2010)

5 Non-Patent Document 3: Z. Anorg. Allg. Chem., 631, 55-59
(2005)

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

[0006]

10 Heating to a temperature of 80°C is required to complete
the reaction among sulfamic acid, thionyl chloride and
chlorosulfonic acid. The boiling point of thionyl chloride
used as a chlorinating agent is 76°C. If the temperature of
a mixture containing thionyl chloride is raised to 80°C or higher,
15 the thionyl chloride evaporates and is eliminated from the
reaction system in the form of thionyl chloride. Consequently
it is necessary to add an excess of thionyl chloride to the
reaction system. Therefore, a method has been attempted that
consists of lowering the temperature early in the reaction and
20 raising the temperature late in the reaction. According to this
method, although the loss of thionyl chloride is reduced, since
a large amount of gas may be generated rapidly such as when
switching from the initial reaction temperature to the final
reaction temperature, this method was unsuitable for use as an

industrial production method.

[0007]

An object of the present invention is to provide an industrially advantageous method for producing
5 bis(halosulfonyl)amine that makes it possible to inhibit rapid generation of gas and reduce the amount of halogenating agent used by controlling the reaction rate among sulfamic acid, a halogenating agent and a halosulfonic acid to nearly a constant rate from the initial stage to the final stage of the reaction.

10 Means for Solving the Problems

[0008]

As a result of conducting extensive studies to solve the aforementioned problems, the inventors of the present invention completed the aspects of the invention as described below.

15 Namely, the present invention includes the aspects indicated below.

(1) A method for producing bis(halosulfonyl)amine, including heating a mixture containing sulfamic acid and a halosulfonic acid to a temperature higher than room temperature
20 followed by adding a halogenating agent thereto.

(2) The production method described in (1), wherein the temperature higher than room temperature is 50°C to 140°C.

(3) The production method described in (1) or (2), wherein the halogenating agent is added by dividing into a plurality
25 of additions.

(4) The production method described in any one of (1) to (3), wherein the halogenating agent is thionyl chloride.

(5) The production method described in (4), wherein 2 to 3 moles of thionyl chloride are added to 1 mole of sulfamic acid.

5 (6) The production method described in any one of (1) to (5), further including reacting the mixture at a temperature of 50°C to 85°C after adding the halogenating agent.

(7) The production method described in any one of (1) to (5), further including reacting the mixture at a temperature
10 of 86°C to 105°C after adding the halogenating agent.

(8) The production method described in any one of (1) to (5), further including reacting the mixture at a temperature of 106°C to 140°C after adding the halogenating agent.

Effects of the Invention

15 [0009]

Since the production method of the present invention makes it possible to inhibit the rapid generation of gas and reduce the amount of halogenating reagent used by controlling the reaction rate among sulfamic acid, the halogenating agent and
20 a halosulfonic acid to nearly a constant rate from the initial stage to the final stage of the reaction, it is advantageous for the industrial production of bis(halosulfonyl)amine. In addition, according to the production method of the present invention, bis(halosulfonyl)amine can be produced at high yield,

thereby making it advantageous for industrial production.

BEST MODE FOR CARRYING OUT THE INVENTION

[0010]

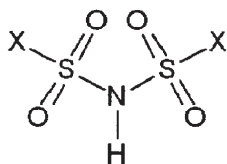
The method for producing bis(halosulfonyl)amine according to one aspect of the present invention includes heating a mixture containing sulfamic acid and a halosulfonic acid to a temperature higher than room temperature following by adding a halogenating agent thereto. Furthermore,

bis(halosulfonyl)amine is a compound represented by formula (3).

In formula (3), X represents halogen atoms. X may be the same or different. Specific examples of bis(halosulfonyl)amines include N-(fluorosulfonyl)-N-(chlorosulfonyl)amine and bis(chlorosulfonyl)amine.

[0011]

[Chemical Formula 1]



(3)

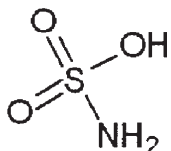
[0012]

The sulfamic acid used in the present invention is a known substance represented by formula (1). A commercially available product may be used for the sulfamic acid. The sulfamic acid is preferably subjected to drying treatment prior to using in the reaction to remove water contained therein. There are no particular limitations on the method used for

drying treatment, and an ordinary method such as heat drying or vacuum drying can be used.

[0013]

[Chemical Formula 2]



5

(1)

[0014]

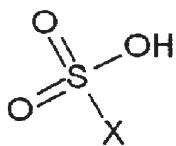
The halosulfonic acid used in the present invention is a known substance represented by formula (2). In formula (2), X represents a halogen atom. A commercially available product may be used for the halosulfonic acid. The halosulfonic acid is preferably subjected to drying treatment prior to using in the reaction to remove water contained therein. There are no particular limitations on the method used for drying treatment, and an ordinary method such as heat drying or vacuum drying can be used. The halosulfonic acid is preferably fluorosulfonic acid or chlorosulfonic acid and more preferably chlorosulfonic acid.

10

15

[0015]

[Chemical Formula 3]



20

(2)

[0016]

There are no particular limitations on the halogenating agent used in the present invention, and a commercially available product can be used. The halogenating agent is preferably subjected to drying treatment prior to using in the reaction to remove water contained therein. There are no particular limitations on the method used for drying treatment, and an ordinary method such as heat drying or vacuum drying can be used. Examples of halogenating agents include phosphorous trichloride, phosphorous pentachloride, thionyl chloride and thionyl fluoride. Thionyl chloride is preferable from the viewpoint of facilitating purification following completion of the reaction.

[0017]

The mixture containing sulfamic acid and a halosulfonic acid is such that the molar ratio of halosulfonic acid to sulfamic acid is preferably 0.9 to 1.2 and more preferably 0.95 to 1.05.

This mixture may also contain a solvent for dissolving or dispersing the sulfamic acid and halosulfonic acid in addition to the sulfamic acid and halosulfonic acid as necessary. Although there are no particular limitations on the solvent provided it does not inhibit the reaction among the sulfamic acid, halogenating agent and halosulfonic acid, it is preferably a compound that does not have an aromatic proton.

[0018]

The mixture containing sulfamic acid and halosulfonic acid is heated prior to addition of the halogenating agent. The temperature of the heated mixture when the halogenating agent is added is a temperature that is higher than room temperature, preferably 50°C to 140°C and more preferably 60°C to 80°C. Adjusting to such a temperature makes it possible to prevent rapid generation of gas.

[0019]

There are no particular limitations on the amount of halogenating agent added. For example, the amount of halogenating agent based on 1 mole of sulfamic acid is preferably 2 to 4 moles and more preferably 2 to 3 moles. If the added amount of halogenating agent is less than 2 moles, yield and purity tend to decrease.

[0020]

Although there are no particular limitations on the manner in which the halogenating agent is added, it may be gradually added continuously, gradually added intermittently or added by dividing into a plurality of additions while providing an interval between each addition.

In the case of adding continuously or intermittently, the addition rate is preferably held to a low rate to prevent sudden increases in the reaction rate. The addition rate can be suitably set according to the size of the reactor and the set reaction temperature. In the case of adding by dividing into

a plurality of additions, the amount added in a single addition is preferably held to a low amount to prevent sudden increases in the reaction rate. The amount added in a single addition can be suitably set according to the size of the reactor and
5 the set reaction temperature.

[0021]

After adding the halogenating agent, the reaction can be allowed to proceed while adjusting the temperature. The temperature of the mixture following addition of the
10 halogenating agent can be set to various temperatures in order to control to a desired reaction rate according to the size of the reactor, and is a temperature higher than room temperature, preferably 50°C to 140°C and more preferably 60°C to 80°C. In addition, the temperature of the mixture following addition of
15 the halogenating agent can be set to, for example, 50°C to 85°C, 86°C to 105°C or 106°C to 140°C.

Although there are no particular limitations on the reaction time, it is normally 48 hours or less and preferably 24 hours or less.

20 [0022]

The reaction can be carried out in the presence of a catalyst. A basic catalyst is preferable for the catalyst. Examples of basic catalysts include aliphatic tertiary amines such as trimethylamine, triethylamine, tripropylamine, tributylamine,

tri(hydroxyethyl)amine, methylpiperidine, dimethylpiperazine or diazabicyclooctane, and trialkylphosphines such as trimethylphosphine or triethylphosphine. The amount of catalyst used is preferably 0.0001 moles to 0.1 moles based on 1 mole of sulfamic acid.

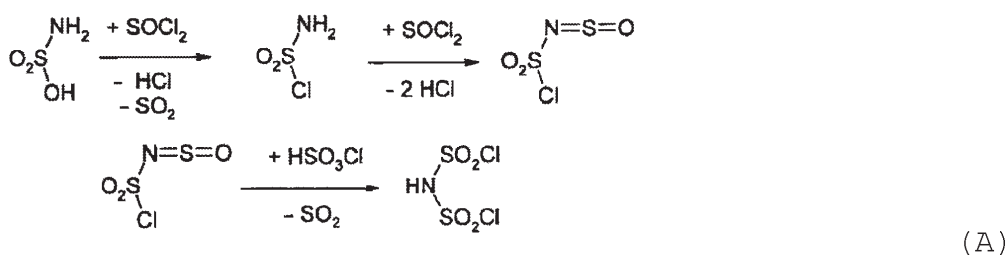
The catalyst may be added to the mixture prior to the addition or the halogenating agent, may be added simultaneous to the addition of the halogenating agent, or may be added following addition of the halogenating agent. Among these, adding to the mixture prior to addition of the halogenating agent is preferable.

[0023]

The sulfamic acid, halogenating agent and halosulfonic acid appear to undergo a reaction represented by reaction scheme (A) or reaction scheme (B) according to Non-Patent Document 3.

[0024]

[Chemical Formula 4]



[0025]

[Chemical Formula 5]

[0026]

In contrast, according to the method of the present invention, rapid generation of gas is inhibited by controlling the reaction rate among the sulfamic acid, halogenating agent and halosulfonic acid to nearly a constant rate from the initial stage to the final stage of the reaction.

[0027]

The following provides a more detailed explanation of the present invention by listing examples thereof. Furthermore,

the present invention is not subjected to limitation by the following examples, and can naturally be carried out by adding suitable modifications within a range that is compatible with the gist of the present invention, and all such modifications are also included within the technical scope of the present invention.

[0028]

Example 1

97.1 g (1.00 mol) of sulfamic acid and 121.2 g (1.04 mol) of chlorosulfonic acid were placed in a 500 ml reaction vessel equipped with a stirrer, thermometer and reflux condenser followed by stirring to obtain a mixture. This mixture was heated to 70°C while stirring. Next, 237.9 g (2.00 mol) of thionyl chloride were dropped therein over the course of 1 hour. The mixture was allowed to react for 6 hours at 70°C. Next, the temperature was raised to 80°C over the course of 0.5 hours. Subsequently, 119.0 g (1.00 mol) of thionyl chloride were dropped in over the course of 1 hour. Next, the temperature was raised to 90°C over the course of 1.9 hours followed by allowing to react for 4 hours at 90°C.

Subsequently, the temperature was raised to 130°C and the reaction was allowed to proceed for 2 hours at 130°C. At this time, unreacted thionyl chloride evaporated and was discharged outside the system.

There was no rapid generation of gas during the
aforementioned reaction.

The resulting reaction liquid was subjected to vacuum
distillation. 206.6 g of a colorless, clear liquid
5 (bis(chlorosulfonyl)amine) was obtained as the fraction
obtained under conditions of 105°C or higher and 7 torr (0.97
mol, yield based on sulfamic acid: 97%, yield based on thionyl
chloride: 32%).

[0029]

10 Example 2

268.0 g (2.76 mol) of sulfamic acid and 334.5 g (2.87 mol)
of chlorosulfonic acid were placed in a 2000 ml reaction vessel
equipped with a stirrer, thermometer and reflux condenser
followed by stirring to obtain a mixture. This mixture was
15 heated to 70°C while stirring. Next, 656.7 g (5.52 mol) of
thionyl chloride were dropped therein over the course of 1.5
hours. Next, the mixture was allowed to react for 6 hours at
70°C. Subsequently, 131.3 g (1.10 mol) of thionyl chloride were
dropped in over the course of 0.2 hours. Next, the temperature
20 was raised to 90°C over the course of 3 hours followed by allowing
to react for 4 hours at 90°C.

Subsequently, the temperature was raised to 130°C and the
reaction was allowed to proceed for 2 hours at 130°C. At this
time, unreacted thionyl chloride evaporated and was discharged

outside the system.

There was no rapid generation of gas during the
aforementioned reaction.

The resulting reaction liquid was subjected to vacuum
5 distillation. 553.6 g of a colorless, clear liquid
(bis(chlorosulfonyl)amine) was obtained as the fraction
obtained under conditions of 100°C or higher and 7.5 torr (2.59
mol, yield based on sulfamic acid: 94%, yield based on thionyl
chloride: 39.1%).

10 [0030]

Comparative Example 1

9.71 g (0.10 mol) of sulfamic acid, 12.12 g (0.104 mol)
of chlorosulfonic acid and 29.74 g (0.25 mol) of thionyl
chloride were placed in a 500 ml reaction vessel equipped with
15 a stirrer, thermometer and reflux condenser followed by
stirring to obtain a mixture. This mixture was heated to 70°C
while stirring followed by allowed to react for 4 hours at 70°C.

The temperature was raised to 130°C over the course of 2
hours followed by allowing to react for 2 hours at 130°C. Gas
20 was rapidly generated during the time the temperature was raised
to 130°C.

The resulting reaction liquid was subjected to vacuum
distillation. 7.74 g of a colorless, clear liquid
(bis(chlorosulfonyl)amine) was obtained as the fraction

obtained under conditions of 110°C or higher and 7 torr (0.036 mol, yield based on sulfamic acid: 36%, yield based on thionyl chloride: 14.4%).

[0031]

5 On the basis of the above results, according to the method of the present invention, bis(halosulfonyl)amine was determined to be able to be produced at high yield while inhibiting rapid generation of gas. In addition, the amount of halogenating agent used relative to the yield of
10 bis(halosulfonyl)amine was determined to be able to be reduced considerably.

INDUSTRIAL APPLICABILITY

[0032]

Since the production method of the present invention makes
15 it possible to inhibit the rapid generation of gas and reduce the amount of halogenating agent used by controlling the reaction rate among sulfamic acid, a halogenating agent and a halosulfonic acid to nearly a constant rate from the initial stage to the final stage of the reaction, it is advantageous
20 for the industrial production of bis(halosulfonyl)amine.

CLAIMS

1. A method for producing bis(halosulfonyl)amine, comprising: heating a mixture containing sulfamic acid and a halosulfonic acid to a temperature higher than room temperature followed by adding a halogenating agent thereto.
2. The production method according to claim 1, wherein the temperature higher than room temperature is 50°C to 140°C.
3. The production method according to claim 1 or 2, wherein the halogenating agent is added by dividing into a plurality of additions.
4. The production method according to any one of claims 1 to 3, wherein the halogenating agent is thionyl chloride.
5. The production method according to claim 4, wherein 2 to 3 moles of thionyl chloride are added to 1 mole of sulfamic acid.
6. The production method according to any one of claims 1 to 5, further comprising reacting the mixture at a temperature of 50°C to 85°C after adding the halogenating agent.
7. The production method according to any one of claims 1 to 5, further comprising reacting the mixture at a temperature of 86°C to 105°C after adding the halogenating agent.
8. The production method according to any one of claims 1 to 5, further comprising reacting the mixture at a temperature of 106°C to 140°C after adding the halogenating agent.