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3,591,471

PREPARATION OF NITROSODISULFONATE

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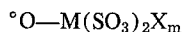
11 Claims

ABSTRACT OF THE DISCLOSURE

Preparation of nitrosodisulfonate by electrolysis of an aqueous solution of hydroxylamine disulfonate.

BACKGROUND OF THE INVENTION

In the past, nitrosodisulfonate of the formula



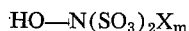
(I)

wherein X is an ammonium ion, alkali metal or alkaline earth metal and m is 1 or 2, with the proviso that when X is an ammonium ion or monovalent metal, m is 2, and when X is a divalent metal, m is 1

a commercial oxidizing agent, has been produced by treating hydroxylamine disulfonate with strong oxidizing agents such as lead dioxide, silver oxide and potassium permanganate. This oxidation procedure has proven to be rather costly due to the expense of these oxidizing agents. Furthermore, during the reaction, the oxidizing agents are reduced to solid metal oxides which contaminate the nitrosodisulfonate. Additionally, these processes suffer from the disadvantage that the nitrosodisulfonate has only been obtained in yields of about 50 to 65 percent. Therefore, it has long been desired to produce a simple and economic process for producing nitrosodisulfonate.

SUMMARY OF THE INVENTION

In accordance with this invention, a nitrosodisulfonate of Formula I above can be produced in almost quantitative yields from a hydroxylamine disulfonate of the formula



(II)

wherein X and m are as above

by subjecting an aqueous medium containing the hydroxylamine disulfonate of Formula II above to electrolysis. This process provides the nitrosodisulfonate of the Formula I above in high yields without any danger of contamination from metal oxides. Additionally, another advantage of this process is that the hydroxylamine disulfonate of Formula II above, which is prepared from sulfur dioxide and an alkali metal nitrite or alkaline earth metal nitrite, need not be isolated from its reaction medium, but can be directly converted by electrolysis to the nitrosodisulfonate of Formula I above. In this manner, a process is provided for directly converting the reaction product of sulfur dioxide with an alkali metal nitrite or alkaline earth metal nitrite into the nitrosodisulfonate of Formula I above without the necessity of isolating any intermediates. Therefore, the process of this invention provides a simple and economical method for producing the nitrosodisulfonate of Formula I above.

DETAILED DESCRIPTION OF THE INVENTION

In the hydroxylamine disulfonate of Formula II above, X can be any conventional alkali metal or alkaline earth metal. Among the conventional alkali metals which X can designate are included sodium, potassium, lithium, rubidium, etc. Among the alkaline earth metals which are designated by X are included magnesium, calcium, etc.

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The reaction of this invention is carried out by electrolytically treating an aqueous reaction medium containing the hydroxylamine disulfonate of Formula II above. This reaction can take place by any conventional electrolytic process.

This process is carried out in a conventional electrolytic cell. In accordance with the present invention, an aqueous solution containing the hydroxylamine derivative of Formula II above is placed in an electrolytic cell, e.g., an electrolysis tank which may or may not be provided with a cell divider or membrane, and which is provided with an anode and a cathode. The cathode and the anode can be made of any material commonly employed for making cathodes and anodes in the electro-chemical art, e.g., carbon, monel, stainless steel, platinum, palladium, nickel, nickel-alloy, etc. The electrolytic cell can be provided with a stirrer or mechanical agitator, or the reaction medium can be circulated by means of pumps. The electrolysis can be carried out by applying voltages of from 0.5 to 50 volts to the liquid aqueous reaction medium. Generally, it is preferred to carry out the reaction utilizing from 5 to 25 volts. The electric current passed through the solution can be of a current density of up to 50 amperes per square decimeter and can be as low as 0.01 ampere per square decimeter. Generally, it is preferred to utilize a current density of from 0.02 to 5 amperes per square decimeter.

In carrying out the electrolysis reaction more efficaciously, a conventional electrolyte can be added to the aqueous medium. Among the conventional electrolytes which can, if desired, be added to the liquid aqueous reaction medium prior to electrolysis are included, sodium hydroxide, acetic acid, sodium acetate, sodium carbonate, sodium bicarbonate, sodium phosphates, sodium chloride, etc. Generally, it is preferred to add the electrolyte in an amount of from 0.1 percent to 30 percent by weight of the liquid medium. During the electrolysis, the pH of the reaction medium is maintained at 4 or above. Optimally this reaction is carried out at a pH of from 4 to 13. The aforementioned electrolytes can be utilized to obtain the desired pH.

The aqueous solution which is subjected to electrolysis generally contains the hydroxylamine derivative of Formula II above in a concentration of at least 0.1 mole per 1,000 ml., preferably from 0.1 mole to 2 moles per 1,000 ml. of solution. The electrolysis reaction can be carried out at any temperature of from -15°C . to 50°C . Generally it is preferred to carry out this reaction at a temperature of -10°C . to $+10^{\circ}\text{C}$. The electrolysis reaction can be carried out for a period of at least $\frac{1}{2}$ hour or longer. Generally, it is preferred to carry out the electrolysis for a period of from 1 to 10 hours. If desired, electrolysis can be carried out for periods longer than 10 hours. However, since the use of electrolysis time of greater than 10 hours produces no additional beneficial results, these prolonged reaction times are seldom employed.

In accordance with an embodiment of this invention the hydroxylamine of Formula II above can be prepared by reacting an alkali metal or alkaline earth metal nitrite with sulfur dioxide in an aqueous medium. In carrying out this reaction, the sulfur dioxide can be bubbled in as a gas into the aqueous reaction medium. Alternatively, the reaction medium can contain any source capable of liberating sulfur dioxide such as a mixture of an organic acid such as acetic acid and an alkali metal or alkaline earth metal bisulfite or sulfite. The nitrite salt and sulfur dioxide or sulfur dioxide liberating source are reacted together at a temperature of from -15°C . to 50°C . to produce the hydroxylamine disulfonate of Formula II above, with -10°C . to $+10^{\circ}\text{C}$. being preferred. This reaction is carried out by reacting 1 mole of the nitrite salt with 2 moles of the sulfur dioxide which can be either bubbled or liberated from the sulfur dioxide liberating

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source in water. Furthermore, this reaction is carried out at a pH of at least 2, preferably, from 2 to 4. This pH is obtained by the addition of acetic acid or other lower alkanic acids to the reaction medium when these acids are utilized as a component of the sulfur dioxide liberating material. However, this pH can be obtained by the addition of weakly basic inorganic salts such as sodium phosphates, sodium carbonates, sodium bicarbonates, etc. This aqueous reaction medium containing the hydroxylamine disulfonate can be directly subjected to electrolysis to form the nitrosodisulfonate of Formula I above without isolating the hydroxylamine disulfonate of Formula II above.

Alternatively, the hydroxylamine of Formula II can be prepared by reacting ammonium nitrite with sulfur dioxide in the aforementioned manner. Furthermore, ammonium bisulfite or sulfite can be utilized in place of alkali metal or alkaline earth metal sulfite or bisulfite in forming sulfur dioxide.

The aqueous reaction medium which is produced by electrolysis contains the compound of Formula I in solution. This reaction medium can be utilized as an oxidizing medium. Alternatively, the compound of Formula I can be recovered in solid form by conventional crystallization techniques such as by treating the aqueous reaction medium with a saturated solution of an alkali metal salt.

This invention will be more fully understood from the specific example which follows. This example is intended to illustrate the invention and is not to be construed as limitative thereof. The temperatures utilized in this example are in degrees centigrade.

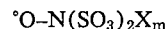
EXAMPLE

A solution of 13.8 g. (0.2 M) sodium nitrite in 100 cc. of water was stirred in an ice bath. 150 g. of ice and 41.6 g. (0.4 M) sodium bisulfite were added. After the salts had dissolved, 22.5 cc. (0.4 M) of acetic acid was added and the water clear solution was stirred at a maximum of 2° C. for one hour. At the end of the stirring period, 200 cc. of saturated sodium carbonate solution was added. The resulting hydroxylamine disulfonate solution showed a pH of 8 and was now anodically oxidized using a stainless steel anode (ca. 16 mesh/cm.) in the form of a sieve which was separated from the cathode compartment by a porous plate diaphragm (cathode material: stainless steel). The oxidation was carried out under continuous stirring at 0° C. at 7-12 v./1 amp. The current density was 0.05 ampere per square decimeter. After ca. 5.5-6 hours, there resulted a deep violet solution of sodium nitrosodisulfonate. To this solution there was added an aqueous saturated solution of potassium chloride. After this addition of potassium chloride, the product, potassium nitrosodisulfonate crystallized from the solution. The yield of this product was about 90 percent.

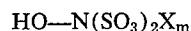
What is claimed is:

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1. A process of producing a nitrosodisulfonate of the formula



wherein X is an ammonium ion, alkali metal or alkaline earth metal and m is 1 or 2, with the proviso that when X is an ammonium ion or monovalent metal, m is 2, and when X is a divalent metal, m is 1 comprising subjecting an aqueous medium containing a hydroxylamine disulfonate of the formula



wherein X and m are as above at a pH of 4-13 to electrolytic oxidation.

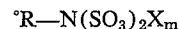
2. The process of claim 1 wherein said electrolysis is carried out at a voltage of from 0.5 to 50 volts.

3. The process of claim 1 wherein X is sodium.

4. The process of claim 1 wherein X is potassium.

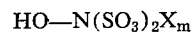
5. The process of claim 1 wherein said aqueous solution contains from about 0.1 to 2 moles of said hydroxylamine per 1000 ml. of water.

6. A process for producing a nitrosodisulfonate of the formula



wherein X is an ammonium ion, alkali metal or alkaline earth metal and m is 1 or 2, with the proviso that when X is an ammonium ion or monovalent metal, m is 2, and when X is a divalent metal, m is 1.

comprising reacting an alkali metal or alkaline earth metal nitrite with sulfur dioxide in an aqueous medium to produce an aqueous solution containing a hydroxylamine of the formula



wherein X and m are as above at a pH 4-13 and subjecting said aqueous solution to electrolytic oxidation to form said nitrosodisulfonate.

7. The process of claim 6 wherein said electrolysis is carried out at a voltage of from 0.5 to 50 volts.

8. The process of claim 6 wherein X is sodium.

9. The process of claim 6 wherein X is potassium.

10. The process of claim 6 wherein said aqueous solution contains from about 0.1 to 2 moles of said hydroxylamine per 1000 ml. of water.

11. The process of claim 6 wherein said sulfur dioxide is produced in the aqueous medium by the reaction of acetic acid with an alkali metal or alkaline earth metal sulfite or bisulfite.

References Cited

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FREDERICK C. EDMUNDSON, Primary Examiner

U.S. Cl. X.R.

23-101, 114

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,591,471 Dated July 6, 1971

Inventor(s) Pius Anton Wehrli

It is certified that error appears in the above-identified patent
and that said Letters Patent are hereby corrected as shown below:

Column 4, line 24 in claim 6

" $\text{°R-N(SO}_3)_2\text{X}_m$ "

should be

$\text{°O-N(SO}_3)_2\text{X}_m$

Signed and sealed this 4th day of January 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Patents