Patented Jan. 12, 1943 2,307,929

UNITED STATES PATENT OFFICE

2,307,929

PREPARATION OF HYDROXYLAMINE

Robert M. Joyce, Jr., Wilmington, Del., assignor to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application May 25, 1940, Serial No. 337,204

12 Claims. (Cl. 23—190)

This invention relates to a process for the preparation of hydroxylamine, and more particularly to its preparation by the pyrolysis of esters of nitrous acid wherein the nitrous acid residue is attached to aliphatic carbon.

Hydroxylamine is well known for its ability to react with a large variety of organic compounds, such as aldehydes, ketones, esters, acid anhydrides, acyl halides, amides, nitriles, etc., to react with both oxidizing and reducing agents, and to form complexes with a great many inorganic salts. So versatile a reagent would be expected to find a wide application in the production of useful products. However, because hydroxylamine has not heretofore been available at an industrially feasible price, it has enjoyed almost no commercial application, and the multitude of compounds derivable from it have received little attention. Likewise, uses for hydroxylamine dependent on its oxidizing or reducing power, or on the intrinsic properties of hydroxylamine have not been fully explored, much less exploited, for the same reason.

It is an object of this invention to provide a radically new process for the production of hydroxylamine which overcomes the disadvantages of previous known methods and by means of which pure hydroxylamine can be prepared economically and at a low cost. Because of the number of potential applications of cheap hydroxylamine, the importance of this invention is at once apparent.

Hydroxylamine has been prepared by the reduction of inorganic nitrites, for example, by bisulfites, by the electrolysis of a mixture of nitric and hydrochloric acids, and by the hydrolysis of aliphatic nitro compounds. Each of these methods entails certain economic disadvantages, such as the production of large quantities of solid by-products whose disposal is difficult, the use of considerable costly equipment, and expensive raw materials.

It has now been discovered that hydroxylamine is produced by subjecting to pyrolysis at elevated temperatures, preferably above 200° C., esters of nitrous acid wherein the nitrous acid residue is attached to aliphatic carbon. This is a most surprising result and totally unpredictable, especially in the light of the known thermal instability of hydroxylamine. For example, in Mellor's "Comprehensive Treatise on Inorganic and Theoretical Chemistry," volume VIII, p. 285 (Longmans, Green and Company, London, 1928), it is noted: ". . . At ordinary pressures hydroxylamine gradually decomposes if kept above 15° C., and at higher temperatures it is liable to explode with a yellow flash. . . ". It is further stated on page 286, quoting J. W. Bruhl: ". . . Decomposition (of hydroxylamine) commences at about 10° C. with the formation of small bubbles of gas, mostly nitrogen; the decomposition at about 20° C. proceeds steadily, and this the faster, the higher the temperature. . . ". Accordingly, it would not have been expected that hydroxylamine could be produced by any reaction taking place at a temperature as high as 200° C.

However, the hydroxylamine produced by the pyrolysis of these nitrous acid esters forms stable derivatives with other products of the pyrolysis, being thereby protected from the otherwise expected decomposition. According to the process of this invention, the pyrolysis products may be cooled and pure hydroxylamine salts isolated therefrom with ease, in accordance with methods such as those described hereinafter. Among the nitrous acid esters which may be employed according to this invention are such aralkyl esters as benzyl and beta-phenylethyl nitrites; such cycloaliphatic esters as methyl cyclohexyl nitrite and the nitrous acid ester of cyclohexyl carbinol; and such aliphatic alkyl esters as tertiary butyl, secondary butyl, n-hexyl, isopropyl, and isoamyl nitrites in addition to those mentioned in the examples.

It is apparent that the process of the present invention is not subject to the disadvantages of previously known processes for the preparation of hydroxylamine. It involves the use of cheap and readily available raw materials—an alcohol and oxides of nitrogen. The process itself is simple, requires little equipment, and is admirably adapted to continuous operation. The isolation of pure hydroxylamine salts or derivatives from the reaction products is a simple and inexpensive operation, and does not involve the concurrent production of difficulty disposable by-products.

In the preceding broad description of this invention, a minimum preferred temperature of 200° C. has been mentioned. It should, additionally, be understood that the temperature limitation for the process of this invention depends to some extent upon the nature of the nitrite being employed. Thus, for methyl nitrite the lower temperature limit for reaction appears to be about 200° C. The upper temperature limit appears, generally, to be that at which secondary reactions become so pronounced as to make the process uncontrollable; in the case of methyl nitrite, this value lies above 430° C., but is dependent upon the space velocity in any given case.

Best results with methyl nitrite have been obtained in the more restricted temperature range of 300–430° C.

There is also an interrelationship between temperature and space velocity in obtaining best results in the process of this invention, i. e., for any given temperature it is advantageous, although not essential, that the space velocity be low enough that all of the nitrite is decomposed in its passage through the reaction vessel and that none appears unchanged in the reaction products. Still lower space velocities, i. e., the allowance of a longer contact time than is necessary for complete decomposition, do not appear to exercise any disadvantageous effect upon the course of the reaction. By "space velocity," as used herein, is meant the volume of vapor (corrected to 0° C.) per volume of reactor per hour.

The process of this invention may be carried out at pressures ranging from a few millimeters of mercury to at least 50 atmospheres. However, because the hydroxylamine-producing reaction is a free space reaction, it is preferred to operate at or below atmospheric pressure.

Although the process of this invention is applicable to the preparation of hydroxylamine from the esters of nitrous acid broadly, such as hereinbefore described, it has been found that the process is particularly successful when applied to esters of nitrous acid having a hydrogen on the carbon bearing the nitrite group. As an even more specific embodiment of this invention, the preferred class of materials used according to the process of this invention is that of the alkyl nitrites, and particularly, the alkyl nitrites in which the alkyl radical thereof contains from 1 to 6 carbon atoms. This preference is due primarly to:

(*a*) Availability and low cost of the alcohols;
(*b*) Ease of esterification;
(*c*) Volatility and resultant ease in handling of the nitrous acid ester; and
(*d*) Relatively high yields of hydroxylamine upon pyrolysis.

Of this class of materials, i. e. alkyl nitrites in which the alkyl radical contains from 1 to 6 carbon atoms, methyl nitrite appears most desirable. On a molar basis this is the cheapest of all alkyl nitrites; it is a gas at ordinary temperatures and, therefore, readily handled under the conditions set forth in the process of this invention, and, finally, the pyrolysis of methyl nitrite is characterized by greatest freedom from undesirable side reactions of any of the alkyl nitrites. Furthermore, hydroxylamine hydrochloride may be isolated directly from a quench solution of the products of the pyrolysis of methyl nitrite as described in the examples.

The following examples illustrate how the invention may be practiced. Parts are by weight unless otherwise indicated. Space velocities are calculated as c. c. of vapor (corrected to 0° C.) per hour per cc. of reactor volume.

Example I

A 0.5" Pyrex glass reactor tube with a volume of approximately 30 cc., empty except for a thermocouple well, is connected with a reservoir containing ice cold water. The reactor is heated to 300° C., flushed with nitrogen, and methyl nitrite then sucked through at a space velocity of approximately 4000 by applying a partial vacuum to the system. The resulting aqueous quench solution gives a positive test for hydroxylamine when treated with ethanol, benzoyl chloride, and ferric chloride.

Example 2

A Pyrex glass reactor ½" x 10", with a thermocouple well, is heated to a temperature of 280° C. while being flushed with nitrogen. The nitrogen is stopped and methyl nitrite is passed in at a space velocity of approximately 2300: the off-gases are conducted into a reservoir containing ice water, then through a trap cooled in Dry Ice and acetone. The temperature of the reactor is maintained at 270–290° C. for the duration of the reaction. A total of 190 parts of methyl nitrite is passed in, and 130 parts of unreacted methyl nitrite is recovered in the Dry Ice-acetone trap. The aqueous quench solution gives a positive test for hydroxylamine; it is analyzed by oxidizing a sample with acidified ferric ammonium sulfate and measuring the evolved nitrous oxide. The analysis indicates a total of 3.4 parts of hydroxylamine in the solution.

Example 3

A Pyrex glass tube of 2.5" inside diameter is heated along twelve inches of its length by an electric furnace, with a slow current of nitrogen passing through it, until the internal temperature is 347° C. Methyl nitrite is then passed through at a space velocity of 41, and the off-gases are quenched in 3100 parts of ice cold methanol. In the first three minutes of the reaction the internal temperature rises to 383–387° C., where it remains for the duration of the reaction. The methyl nitrite supply is shut off when 154 parts has been passed in; the system is then flushed thoroughly with nitrogen. The quenching solution is treated with dry hydrogen chloride gas and concentrated by distilling through an efficient fractionating column. When the distillate no longer contains formaldehyde, the still pot residue is evaporated to dryness on a steam bath, yielding 23 parts of pure hydroxylamine hydrochloride.

Example 4

A reactor made of 2½" iron pipe is heated along twelve inches of its length to an internal temperature of 352° C. (thermocouple well 3½" from top of furnace) while a slow current of nitrogen is passed through. The nitrogen is cut off, and 290 parts of methyl nitrite is passed through the reactor at a space velocity of 50. The reaction products are quenched in 3100 parts of cold methanol. At the end of the reaction, the system is flushed with nitrogen, and the methanol solution then treated with dry hydrogen chloride gas and concentrated through an efficient fractionating column. When the distillate no longer contains formaldehyde, the still pot residue is evaporated to dryness over steam, yielding 37 parts of hydroxylamine hydrochloride.

Example 5

A Pyrex glass reactor ½" x 10", equipped with a thermocouple well, is heated to 328° C. while being flushed with nitrogen. The current of nitrogen is then passed through a reservoir containing ethyl nitrite so as to carry vapors of the latter through the reactor; the off-gases are quenched in cold methanol. The reaction temperature rises to 336° C. in three minutes, and is maintained at 336–342° C. for the duration of the reaction. Hydroxylamine is formed, and is found in the methanol quench solution.

Example 6

A Pyrex glass reactor ½'' x 10'', equipped with a thermocouple well, is heated to a temperature of 352° C. while being flushed with nitrogen. Isopropyl nitrite is introduced into the system by dropping mercury into a reservoir containing the liquid ester; the latter is passed into a steam heated vaporizer, the vapor then passed through the reactor, and the off-gases finally quenched in ice water. The space velocity of the isopropyl nitrite vapor is approximately 1300. The reaction temperature falls to 338° C. in two minutes, and remains at this figure for the duration of the reaction. A total of 175 parts of the nitrite is added. The resultant aqueous solution gives a positive test for hydroxylamine by the benzoyl chloride-ferric chloride procedure; it is analyzed by oxidation with acidic ferric sulfate and measurement of the evolved nitrous oxide. There is found present a total of 17 parts of hydroxylamine.

Example 7

n-Butyl nitrite is pyrolyzed with the same setup and procedure as that described in the preceding experiment. The reaction temperature is 327–342° C.; the space velocity of the butyl nitrite vapor is approximately 940. Analysis of the aqueous quench solution indicates a yield of 12 parts of hydroxylamine from 172 parts of butyl nitrite.

Example 8

A ½'' x 10'' Pyrex tube equipped with a thermocouple well is heated to a temperature of 338° C. and flushed with nitrogen. A partial vacuum is applied to the system, and 180 parts of cyclohexyl nitrite is passed through the reactor by bleeding a current of nitrogen through a reservoir containing the ester while warming the reservoir slightly on a steam bath. The off-gases are quenched in water; the aqueous solution is extracted with ether to remove a water-insoluble yellow oil. The resulting aqueous extract gives a positive test for hydroxylamine with benzoyl chloride and ferric chloride; it is analyzed by oxidation with ferric sulfate and measurement of the evolved nitrous oxide, and found to contain 4 parts of hydroxylamine.

Although quenching agents have been disclosed in the examples, no such agent is essential to the successful operation of this process; for example, hydroxylamine may be isolated from the product obtained by condensing the off-gases from the pyrolysis against a cold surface. It is often convenient, however, to use an inert liquid agent for quenching or condensing the reaction products, such as water or an alcohol, for example methyl, ethyl, propyl and like alcohols.

A large proportion of the nitrogen of the nitrous acid ester which is not converted to hydroxylamine appears in the pyrolysis products as nitric oxide; this may be partially oxidized and the product used for the conversion of more alcohol to its nitrous acid ester, thereby increasing the efficiency of the process.

Various changes may be made in the details and preferred embodiments of this invention without departing therefrom or sacrificing any of the advantages thereof.

I claim:

1. A process for the production of a hydroxylamine salt which comprises subjecting to pyrolysis at an elevated temperature and below the temperature of decomposition of the hydroxylamine compound which is formed, an organic nitrite wherein the nitrite radical is attached to an alkyl radical containing from 1 to 6 carbon atoms, collecting the reaction products containing hydroxylamine in combined form and reacting with a mineral acid to form the hydroxylamine salt of the acid.

2. The process for the production of a hydroxylamine salt which comprises subjecting to pyrolysis at a temperature of at least 200° C. and below the temperature of decomposition of the hydroxylamine compound which is formed, an organic nitrite wherein the nitrite radical is attached to an alkyl radical containing from 1 to 6 carbon atoms, collecting the reaction products containing hydroxylamine in combined form and reacting with a mineral acid to form the hydroxylamine salt of the acid.

3. The process for the production of a hydroxylamine salt which comprises subjecting to pyrolysis at a temperature in the range of 300 to 430° C. an organic nitrite wherein the nitrite radical is attached to an alkyl radical containing from 1 to 6 carbon atoms, collecting the reaction products containing hydroxylamine in combined form and reacting with a mineral acid to form the hydroxylamine salt of the acid.

4. A process for the production of a hydroxylamine salt which comprises subjecting to pyrolysis at a temperature of at least 200° C. and below the temperature of decomposition of the hydroxylamine compound which is formed, an organic nitrite wherein the nitrite radical it attached to aliphatic carbon, cooling the resultant product in a quenching solution, adding a mineral acid, and isolating the hydroxylamine salt of the acid.

5. A process for the production of a hydroxylamine salt which comprises subjecting to pyrolysis at a temperature of at least 200° C. and below the temperature of decomposition of the hydroxylamine compound which is formed, an organic nitrite wherein the nitrite radical is attached to aliphatic carbon and having a hydrogen atom on the carbon bearing the nitrite group, cooling the resultant product in a quenching solution, adding a mineral acid, and isolating the hydroxylamine salt of the acid.

6. A process for the production of a hydroxylamine salt which comprises subjecting to pyrolysis at a temperature of at least 200° C. and below the temperature of decomposition of the hydroxylamine compound which is formed, an organic nitrite wherein the nitrite radical is attached to an alkyl radical containing from 1 to 6 carbon atoms, cooling the resultant product in a quenching solution, adding a mineral acid and isolating the hydroxylamine salt of the acid.

7. A process for the production of a hydroxylamine salt which comprises subjecting to pyrolysis, at an elevated temperature and below the temperature of decomposition of the hydroxylamine compound which is formed, an organic nitrite wherein the nitrite radical is attached to aliphatic carbon, collecting the reaction products containing hydroxylamine in combined form and reacting these reaction products with a mineral acid to form the hydroxylamine salt of the acid.

8. A process for the production of a hydroxylamine salt which comprises subjecting to pyrolysis, at an elevated temperature and below the temperature of decomposition of the hydroxylamine compound which is formed, an organic nitrite wherein the nitrite radical is attached to aliphatic carbon and having a hydrogen atom on the carbon bearing the nitrite radical, collecting the reaction products containing hy-

droxylamine in combined form and reacting these reaction products with a mineral acid salt to form the hydroxylamine salt of the acid.

9. A process for the production of a hydroxylamine salt which comprises subjecting to pyrolysis, at a temperature of 300 to 430° C., an organic nitrite wherein the nitrite radical is attached to aliphatic carbon and having a hydrogen atom on the carbon bearing the nitrite radical, collecting the reaction products containing hydroxylamine in combined form and reacting these reaction products with a mineral acid salt to form the hydroxylamine salt of the acid.

10. A process for the production of a hydroxylamine salt which comprises subjecting methyl nitrite to pyrolysis at an elevated temperature, and below the temperature of decomposition of the hydroxylamine compound which is formed, collecting the reaction products containing hydroxylamine in combined form and reacting with a mineral acid to form the hydroxylamine salt of the acid.

11. A process for the production of a hydroxylamine salt which comprises subjecting ethyl nitrite to pyrolysis at an elevated temperature, and below the temperature of decomposition of the hydroxylamine compound which is formed, collecting the reaction products containing hydroxylamine in combined form and reacting with a mineral acid to form the hydroxylamine salt of the acid.

12. A process for the production of a hydroxylamine salt which comprises subjecting n-butyl nitrite to pyrolysis at an elevated temperature, and below the temperature of decomposition of the hydroxylamine compound which is formed, collecting the reaction products containing hydroxylamine in combined form and reacting with a mineral acid to form the hydroxylamine salt of the acid.

ROBERT M. JOYCE, JR.