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PRODUCTION OF HYDROXYLAMMONIUM SALTS

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My invention relates to the production of hydroxyl-ammonium salts, and more specifically to an improved process for the production of hydroxylammonium salts by the action of strong acids on primary nitroalkanes.

Hydroxylammonium salts are produced simultaneously with fatty acids by the reaction of strong acids on nitroalkanes. The production of these products from nitroalkanes by the use of mineral acids, sulfonic acids, and alpha-halogenated fatty acids, is disclosed in U. S. Patents 2,113,812, 2,113,813, and 2,113,814, of S. B. Lippincott. In accordance with the procedures of these patents, there is theoretically produced an equimolecular mixture of fatty acid and hydroxylammonium salt. However, this theoretical yield of hydroxylammonium salt has not been achieved in practice. Yields ranging from 70–85% of the theoretical yield have usually been obtained, and up to the present time no procedure has been designed for consistently obtaining yields higher than this. No adequate explanation for the low yields of hydroxylammonium salt, as compared to the obtainable yields of fatty acid, has been advanced, although it has been thought that such low yields may have been caused, in part, by the oxidizing effect of the strong acid used for the conversion.

I have now found that the low yields of hydroxylammonium salts, previously obtained in this process, have been caused by the adverse effect of traces of iron in the reaction mixture, and that this effect is particularly pronounced near the reflux temperature of the reaction mixture. I have further found that the iron tolerance of such mixtures at a given reaction temperature is directly proportional to the chain length of the nitroparaffin, but is inversely proportional to the reflux temperature of the particular mixture employed. Thus, for example, an aqueous sulfuric acid-nitroethane mixture at or near its reflux temperature will tolerate as much as 0.005% by weight of iron and still be capable of producing the hydroxylammonium salt in yields of 90% and above, whereas under comparable conditions similar results can be obtained with 1-nitropropane, and 1-nitrobutane, whose mixtures contain iron to the extent of about 0.0005% and 0.0002% by weight of iron respectively.

Iron contamination of such mixtures usually originates from either one of two sources, i. e., the nitroalkane or the acid. The nitroalkanes have a slight corrosive action on ferrous metal surfaces, particularly in the presence of any moisture, and the handling and storing of these materials in ordinary iron or steel equipment will result in contamination with iron sufficient to affect the yield of hydroxylammonium salt in this process. Likewise, the usual acids employed for converting the nitroalkanes into fatty acids and hydroxylammonium salts, contain iron in sufficient quantity to decrease the yield of hydroxylammonium salt in this process. For example, in the case of sulfuric acid, even when iron content is included in specifications for battery acid or acid for use in the textile industries, the usual limit of iron content is 0.01% ("Sulfuric Acid Manufacture," A. M. Fairlie, Reinhold Publishing Corporation, 1936, page 289).

When concentrated acid is used for the conversion of the nitroalkane, additional water must be added to the reaction mixture to supply the equimolecular amount required for complete conversion of the nitroalkanes. In view of the extremely small amounts of iron which can adversely affect the yields of hydroxylammonium salts, this added water is also a possible source of contamination with iron, especially if there is danger of entrained rust particles in the water supply.

In accordance with my invention, therefore, all sources of possible iron contamination should preferably be investigated, and for optimum results the iron should be excluded from the reaction mixture insofar as practically possible. However, improved yields of hydroxylammonium salts are obtainable by reducing the iron content of the reaction mixture, even if it is not attempted to completely exclude iron from the mixture. The removal of the last minute trace of iron from any of the reactants would of course be uneconomical, and, in general, I have found that it is unnecessary to maintain the iron content of the reaction mixture below the concentrations specified above under the conditions described. In any event, however, the effective amount of iron in any reaction mixture should be decreased sufficiently to reduce the adverse effect on the yield of hydroxylammonium salt, when carrying out my present invention. In general, it may be said that the amount of iron in the reaction mixture should not be substantially greater than 0.005% by weight, and sufficiently below this amount to reduce the adverse effect on the yield of hydroxylammonium salt.

The improved process of my present invention is applicable to the production of hydroxylammonium salts from any of the primary nitroalkanes and is especially useful in the conversion of the lower primary nitroalkanes, and particularly in the conversion of nitroethane, 1-nitro-

propane, and 1-nitrobutane by means of sulfuric acid.

With the exception of the reduction of the iron content of the reaction mixture, in accordance with my present process, any of the known procedures for the conversion of primary nitroalkanes to hydroxylammonium salts, may be followed. The procedures of the patents of Lippincott, referred to above, are quite suitable when modified to reduce the iron content of the reaction mixture. However, for optimum yield of hydroxylammonium salt I prefer to employ an excess of nitroalkane, rather than an excess of converting acid, as recommended by Lippincott. I have found that improved yields of hydroxylammoninum salts are obtainable by the use of an excess of nitroalkane of the order of 10–20% in excess of the theoretical equimolecular mixture with converting acid and water. By theoretical equimolecular mixture I mean one mole of nitroalkane, one mole of sulfuric acid and one mole of water as set forth in Lippincott Patent 2,113,812, page 2, column 1, lines 20–23. Various other modifications of the known procedures for effecting this reaction, may also be employed in conjunction with my present invention.

My invention may be further illustrated by the following specific examples:

EXAMPLE I

Mixtures of 100 parts by weight of 1-nitropropane, 10 parts by weight of water, and 100 parts by weight of 66° Bé. sulfuric acid were prepared, using specially-purified materials containing no iron. To these different mixtures, small amounts of ferrous ammonium sulfate were added, and the resulting mixtures were analyzed for iron content. Each of the mixtures was refluxed for 7 hours (reflux temperature approximately 140° C.), at the end of which time the mixture was cooled, and allowed to separate. The lower layer, constituting the crude hydroxylammonium acid sulfate, was drawn off, weighed, and analyzed for hydroxylamine. The iron content of each mixture, and the yield of hydroxylammonium acid sulfate obtained, are shown in the table below:

Table

Iron content of reaction mixture, percent by weight	Yield of hydroxylammonium acid sulfate, percent of theoretical
0.0010	84.5
0.0005	87.0
0.0002	92.0
0.0001	94.5
0.0000	94.5

EXAMPLE II

Iron-free mixtures consisting of 100 parts by weight of nitroethane, 12 parts by weight of water, and 120 parts by weight of 66° Bé. sulfuric acid, were prepared. To these different mixtures, small amounts of ferrous ammonium sulfate were added, and the resulting mixtures were refluxed for 8 hours at 115–125° C. The reaction product in each case was measured and analyzed for hydroxylamine content. The iron content of each mixture, and the yield of hydroxylammonium acid sulfate obtained, are shown in the table below:

Table

Iron content of reaction mixture, percent by weight	Yield of hydroxylammonium acid sulfate, percent of theoretical
0.0063	92.0
0.0015	96.0

EXAMPLE III

Iron-free mixtures consisting of 1.10 moles of 1-nitrobutane, 1.0 mole of sulfuric acid (66° Bé.) and 1.0 mole of water, were prepared. To these different mixtures, weighed amounts of ferrous ammonium sulfate were added to give the desired iron content, and the resulting mixtures refluxed for a period or four hours at a temperature of about 160° C. At the conclusion of the reaction, a total of 700 cc. of water was added to the mixtures, and the unreacted 1-nitrobutane distilled off. The butyric acid in the two-phase distillate was neutralized with sodium carbonate and the volume of 1-nitrobutane recovered, was measured, and the aqueous residues from the distillates analyzed for hydroxylammonium acid sulfate. The iron content of each mixture and the yield of hydroxylammonium acid sulfate obtained were calculated, and are shown in the table below:

Table

Iron content of reaction mixture, percent by weight	Yield of hydroxylammonium acid sulfate, percent of theoretical
0.001	75
0.0005	81
0.0002	88
0.0000	93

It is to be understood, of course, that the above examples are merely illustrative, and do not limit the scope of my invention. As has previously been pointed out, any of the primary nitroalkanes, and any of the known converting acids may be used in this process, and the reaction procedure may be modified in numerous respects as long as the iron content of the reaction mixture is reduced in accordance with my process. In general, it may be said that the use of any modifications of procedure, or any equivalents which would naturally occur to one skilled in the art, is included in the scope of my invention.

My invention now having been described, what I claim is:

1. In a process for the production of hydroxylammonium acid sulfate by the action of sulfuric acid on a primary nitroalkane, the improvements which comprise effecting the reaction at the approximate reflux temperature of the acid-nitroalkane mixture in the presence of from about 10 to 20 per cent excess of nitroalkane over the theoretical equimolecular mixture with sulfuric acid and water, maintaining the iron content of the reaction mixture at a concentration not above 0.005 per cent by weight, and sufficiently below this concentration to reduce the adverse effect of said iron on the yield of hydroxylammonium acid sulfate, and thereafter recovering the hydroxylammonium acid sulfate thus produced.

2. In a process for the production of hydroxylammonium acid sulfate by the action of sulfuric

acid on nitroethane, the improvements which comprise effecting the reaction at the approximate reflux temperature of the mixture in the presence of from about 10 to 20 per cent excess of nitroethane over the theoretical equimolecular mixture with sulfuric acid and water, maintaining the iron content of the reaction mixture at a concentration not above 0.005 per cent by weight, and thereafter recovering the hydroxylammonium acid sulfate thus produced.

3. In a process for the production of hydroxylammonium acid sulfate by the action of sulfuric acide on 1-nitropropane, the improvements which comprise effecting the reaction at the approximate reflux temperature of the mixture in the presence of from about 10 to 20 per cent excess of 1-nitropropane over the theoretical equimolecular mixture with sulfuric acid acid and water, maintaining the iron content of the reaction mixture at a concentration not in substantial excess of 0.0005 per cent by weight, and thereafter recovering the hydroxylammonium acid sulfate thus produced.

4. In a process for the production of hydroxylammonium acid sulfate by the action of sulfuric acid on 1-nitrobutane, the improvements which comprise effecting the reaction at the approximate reflux temperature of the mixture in the presence of from about 10 to 20 per cent excess of 1-nitrobutane over the theoretical equimolecular mixture with sulfuric acid and water, maintaining the iron content of the reaction mixture at a concentration not in substantial excess of 0.0002 per cent by weight, and thereafter recovering the hydroxylammonium acid sulfate thus produced.

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