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MANUFACTURE OF ORGANIC POLYSULFIDES

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The present invention pertains to oxidation of organic compounds having an SM radical, M designating ammonium or substituted ammonium radical, a metal or hydrogen, and S designating sulfur. It was developed primarily as a process for obtaining tetra-alkyl thiuram disulfides by oxidation of salts of dialkyl dithiocarbamic acids and it will accordingly be described first with reference to that problem.

In an article in the Canadian Journal of Research, volume 2, pages 144–52 (1930), Cambron and Whitby have described a process by which a salt of diethyl dithiocarbamic acid is oxidized with a nitrous acid salt at 0° C. by addition of a dilute mineral acid to produce the desired tetraethyl thiuram disulfide, in accordance with the following equation:

$$2(C_2H_5)_2NCSSNa + 2NaNO_2 + 4HCl \longrightarrow (C_2H_5)_2NC(=S)SSC(=S)N(C_2H_5)_2 + 2H_2O + 2NO + 4NaCl$$

Cambron and Whitby discussed this reaction on page 151 of their article, describing an experiment involving treatment of a mixture containing 45 grams of the sodium salt of diethyl dithiocarbamic acid and 18 grams of sodium nitrite in 100 cc. of water with 80 cc. of a 25% hydrochloric acid solution. They noted the fact that the crystallized tetra alkyl thiuram disulfide obtained by this process had a melting point of 71° C. and was a relatively pure product, but made no comment with respect to the conversion or yield obtained in the practice of the process.

As mentioned in the patent to Olin and Deger, 2,325,194, neither the yield nor conversion obtained in practice of the Cambron and Whitby process is particularly high. A substantial improvement in a process of this general character has been made by Olin and Deger, as described and claimed in their Patent 2,325,194, whereby these conversions and yields are much increased. In the practice of the process of said Olin and Deger patent, methyl, ethyl, propyl, isopropyl, butyl, or a higher alcohol is mixed with a nitrous acid salt and the salt of the dialkyl dithiocarbamic acid to be oxidized, and the resultant mixture is cooled while a dilute solution of a mineral acid (e. g., sulfuric, hydrochloric or phosphoric acid) is gradually added. As taught by Olin and Deger, the nitrous acid is believed to be first converted into the corresponding alkyl nitrite and this alkyl nitrite thereafter serves as the oxidizing agent, as illustrated by the following equations:

$$2ROH + 2NaNO_2 + 2HCl \rightleftarrows 2RONO + 2H_2O + 2NaCl$$

$$2RONO + 2NaSCSNR_2 + 2HCl \leftrightarrows R_2NC(=S)SSC(=S)NR_2 + 2ROH + 2NO + 2NaCl$$

In the oxidation of salts of dialkyl dithiocar-

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bamic acids in practice of the present invention, as in practice of the invention of the Olin and Deger patent, it is preferable that an aliphatic alcohol, such as methyl alcohol or one of the other alcohols mentioned above, be employed in addition to the nitrous acid salt and the mineral acid. Regardless of whether an alcohol or alkyl nitrite is employed, however, or whether a mixture of an alkyl nitrite with an inorganic salt of nitrous acid is employed, substantial advantage is obtained by practice of the oxidation reaction in accordance with the modified order of procedure of the present invention.

The present invention rests upon the discovery that, in an oxidation reaction of this type, the formation of the desired organic polysulfide may be substantially improved, from the standpoint of conversion, yield, and economy of materials, by the addition of the mineral acid and the organic compound to be oxidized separately and progressively into an aqueous solution of the oxidizing agent. In the manufacture of tetra-alkyl thiuram disulfides by oxidation of salts of dialkyl dithiocarbamic acids in aqueous solution, for example, it has been found that the yield can be increased considerably, the quantity of aliphatic alcohol required to obtain best results reduced by as much as 75%, and the quantity of oxidizing agent necessary to accomplish the oxidation reduced, by the simple change in procedure involved in maintaining a body of the oxidizing agent and introducing the aqueous solution of dithiocarbamic acid salt and mineral acid separately and progressively into this body of oxidizing agent.

In the practice of the invention, there is first introduced into the reaction vessel an aqueous solution of the oxidizing agent. This oxidizing agent may be an alkyl nitrite, a salt of nitrous acid, or a mixture of a nitrous acid salt with an alkyl nitrite. In accordance with preferrad procedure, a nitrous acid salt and an aliphatic alcohol are introduced into the reaction vessel and serve as the oxidizing medium. Separate aqueous solutions of the dithiocarbamic acid salt to be oxidized (e. g., the sodium salt of diethyl dithiocarbamic acid) and of the mineral acid (hydrochloric acid) are then introduced progressively at such relative rates that the reaction mixture contains a moderate concentration of unoxidized dithiocarbamic acid salt until the final stage of the reaction. In the case of use of a nitrous acid salt as the oxidizing agent and a salt of the dithiocarbamic acid as the material to be oxidized, there will of course be formed two molecules of basic constituents for each molecule of thiuram disulfide formed, and it is, of course, desirable that these basic constituents be entirely neutralized. In practice of the invention, however, it is best that the quantity of mineral acid added

lag somewhat behind the stoichiometric quantity which would be necessary for neutralization of the theoretical quantity of basic constituents formed if the entire body of dithiocarbamic acid salt were to be oxidized; i. e., in the particular case under consideration, the quantity of hydrochloric acid should be less than double the molecular quantity of dithiocarbamic acid salt introduced. After the total quantity of dithiocarbamic acid salt to be oxidized has been introduced, it will, of course, be desirable that the oxidation reaction be carried to completion and the neutralization of liberated basic constituents completed by addition of a further quantity of mineral acid sufficient to accomplish completion of the oxidation and neutralization of the bases liberated incident to such completion.

In line with the discussion of the detailed procedure explained in the last preceding paragraph, it should be pointed out that one excellent way to assure maintenance of a stoichiometric excess of the organic compound to be oxidized, as compared to the mineral acid introduced, is to first introduce a part of the organic compound to be oxidized into the aqueous solution of oxidizing medium, and then to introduce the mineral acid and further material to be oxidized, this subsequent introduction taking place progressively and simultaneously, and in approximately the proportions in which the material to be oxidized and the mineral acid enter into the reactions of oxidation and neutralization with which we are concerned. Thus, in the oxidation of salts of dialkyl dithiocarbamic acids, a minor portion of such salt may first be introduced into the aqueous solution of oxidizing medium, and the remainder may thereafter be introduced simultaneously with the mineral acid, a relative rate of introduction of two moles of mineral acid for each mole of the salt of the dithiocarbamic acid salt being maintained during such subsequent introduction until all of the dithiocarbamic acid salt to be oxidized has been introduced and until the reaction has gone fairly far toward completion. When this stage has been reached, the remainder of the mineral acid necessary to produce the ultimate degree of oxidation and neutralization is then gradually introduced, without further introduction of other reactants.

While the invention has been described above in reference to formation of thiuram disulfiides, it should be understood that this invention is by no means limited to this one specific problem but is applicable generally to organic oxidation reactions of this type, as discussed in the aforementioned Olin and Deger Patent 2,325,194. Thus, the general order of procedure herein discussed may be employed in the manufacture of xanthogen disulfides by oxidation of xanthates, in the manufacture of dithiocarbonic acid, didithiocarbonic acid and di-trithiocarbonic acid from the corresponding mono-, di-, and trithiocarbonic acids, respectively, and in the manufacture of disulfides from mercaptans.

Futhermore, although the invention may advantageously be practiced by the maintenance of a relatively small excess of carbamate during the major part of the oxidation, it is to be understood that the presence of even higher relative concentrations will lead to results which are more favorable than when the entire quantity of oxidizable material is charged initially.

The following examples illustrate the practice of this invention as applied in manufacture of tetra-alkyl thiuram disulfides and will teach the person skilled in the art, when they are considered in conjunction with the examples of the aforesaid Olin and Deger patent, to practice the invention in oxidation of these other sulfhydryl derivatives.

Example I

2 moles of the sodium salt of diethyl dithiocarbamic acid, dissolved in 70 moles of water, were oxidized to form tetra ethyl thiuram disulfide by treatment with 2 moles of sodium nitrite and 4 moles of hydrogen chloride in the presence of one mole of methanol, as follows. To a charge consisting of all the methanol, all the sodium nitrite, and 30% of the sodium diethyl dithiocarbamate dissolved in water there were gradually introduced at uniform rates over a period of one hour aqueous solutions containing all the remainder of the sodium salt of diethyl dithiocarbamic acid and hydrogen chloride. The relative rates of introduction of these subsequently added aqueous solutions was such that an excess of the salt to be oxidized was constantly maintained in the reaction mixture and that the addition of the dithiocarbamic acid salt was completed when only 85% of the theoretically required (double the stoichiometric) amount of hydrogen chloride had been added. The remainder of the necessary hydrochloric acid solution was then added gradually in order to complete the reaction. The reaction mixture was agitated vigorously and cooled during the practice of the process of this example as described above in order to maintain the temperature at approximately 20° C. throughout the reaction. The yield of the desired tetraethyl thiuram disulfide was 99%.

Comparative Example II

This example is given for the purpose of providing a comparison between the process of Olin and Deger Patent 2,325,194, and the process of the present invention. It should be compared to Example III, below. A batch of sodium diethyl dithiocarbamate solution was prepared by the action of diethyl amine on a mixture of carbon disufilde and aqueous caustic soda. 2 moles of this solution (containing 65 moles of water) were charged into a reactor, and 2 moles of sodium nitrite and 2 moles of methanol were added. To this solution, held at 25° C., and agitated, was introduced 4 moles of 66° Bé. HCl over a period of 45 minutes. The yield of tetra ethyl thiuram disulfide was 89%.

Example III

Using the same carbamic acid salt solution as in Example II and the same proportions of reactants, a run was made in which all the nitrite and methanol and 20% of the carbamic acid solution were charged into the reaction vessel. The remaining carbamic acid salt solution and all of the hydrochloric acid were then introduced through separate tubes at uniform rates. The yield of tetra ethyl thiuram disulfide was 95.5%.

Example IV

A run was made which was similar in all respects to that described in Example III, except that one mole of methanol was used instead of two. The yield of tetra ethyl thiuram disulfide was 97%.

Example V

A run was made which was similar in all respects to that described in Example III except that only half of the quantity of methanol and three-quarters of the quantity of sodium nitrite used in that example were employed. The yield of tetra ethyl thiuram disulfide was 91%.

Various modifications are available to those skilled in the art, and I do not therefore wish to be limited except by the scope of the following claims.

I claim:

1. In the manufacture of a thiuram disulfide by the oxidation of a salt of a dialkyl dithiocarbamic acid, the process comprising introducing said salt and a mineral acid separately and progressively into an aqueous solution of an oxidizing agent chosen from the class consisting of salts and alkyl esters of nitrous acid, and mixtures of said salts and esters, the respective rates of introduction of said mineral acid and of said first-mentioned salt being regulated with respect to each other such as to maintain in the reaction mixture an unreacted portion of said first-mentioned salt until such time as the introduction of said first-mentioned salt is discontinued.

2. In the manufacture of a thiuram disulfide by the oxidation of a salt of a dialkyl dithiocarbamic acid, the process comprising introducing said salt and a mineral acid separately and progressively into an aqueous solution of a nitrous acid salt and methyl alcohol, the respective rates of introduction of said mineral acid and of said first-mentioned salt being regulated with respect to each other such as to maintain in the reaction mixture an unreacted portion of said first-mentioned salt until such time as the introduction of said first-mentioned salt is discontinued.

3. In the manufacture of a thiuram disulfide by the oxidation of a salt of a dialkyl dithiocarbamic acid, the process comprising introducing said salt and a mineral acid separately and progressively into an aqueous solution of a nitrous acid salt and an aliphatic alcohol, the respective rates of introduction of said mineral acid and of said first-mentioned salt being regulated with respect to each other such as to maintain in the reaction mixture an unreacted portion of said first-mentioned salt until such time as the introduction of said first-mentioned salt is discontinued.

4. In the manufacture of a thiuram disulfide by the oxidation of a salt of a dialkyl dithiocarbamic acid, the process comprising introducing said salt and a mineral acid separately and progressively into an aqueous solution of an alkyl nitrite, the respective rates of introduction of said mineral acid and of said first-mentioned salt being regulated with respect to each other such as to maintain in the reaction mixture an unreacted portion of said first-mentioned salt until such time as the introduction of said first mentioned salt is discontinued.

5. In the manufacture of a thiuram disulfide by the oxidation of a salt of a dialkyl dithiocarbamic acid, the process comprising introducing a quantity of said salt into an aqueous solution of an aliphatic alchol and an oxidizing agent comprising a salt of nitrous acid, thereafter introducing further quantities of said first-mentioned salt and of a mineral acid separately and progressively into said aqueous solution, the respective rates of introduction of said mineral acid and of said first-mentioned salt being regulated with respect to each other such as to maintain an unreacted portion of said first-mentioned salt until such time as the introduction of said first-mentioned salt is discontinued, and thereafter continuing the addition of said mineral acid to neutralize basic constituents formed incident to the oxidation reaction.

6. In the manufacture of a thiuram disulfide by the oxidation of a salt of a dialkyl dithiocarbamic acid, the process comprising introducing a quantity of said salt into an aqueous solution of an aliphatic alcohol and an oxidizing agent comprising a salt of nitrous acid, and thereafter introducing further quantities of said first-mentioned salt and of a mineral acid separately and progressively into said aqueous solution, the addition of said first-mentioned salt and of said mineral acid being controlled at such rate that the quantity of said first-mentioned salt in the solution is maintained in stoichiometric excess of the quantity of mineral acid in said solution until substantially the entire quantity of said salt to be oxidized has been introduced into said solution.

7. In the manufacture of a thiuram disulfide by the oxidation of a salt of a dialkyl dithiocarbamic acid, the process comprising introducing a quantity of said salt into an aqueous solution of an aliphatic alcohol and an oxidizing agent comprising sodium nitrite, and thereafter introducing further quantities of said first-mentioned salt and of a mineral acid separately and progressively into said aqueous solution, the addition of said first-mentioned salt and of said mineral acid being controlled at such rate that the quantity of said first-mentioned salt in the solution is maintained in stoichiometric excess of the quantity of mineral acid in said solution until substantially the entire quantity of said salt to be oxidized has been introduced into said solution, and a further quantity of the mineral acid being thereafter added until a quantity of mineral acid has been added which is sufficient to neutralize basic constituents formed incident to the oxidation reaction.

8. In the manufacture of tetraethyl thiuram disulfide by the oxidation of a salt of diethyl dithiocarbamic acid, the process comprising introducing said salt and a mineral acid separately and progressively into an aqueous solution of a salt of nitrous acid and a saturated aliphatic monohydric alcohol having less than 5 carbon atoms, the respective rates of introduction of said mineral acid and of said first-mentioned salt being regulated with respect to each other such as to maintain in the reaction mixture an unreacted portion of said first-mentioned salt until such time as the introduction of said first-mentioned salt is discontinued.

9. In the manufacture of tetramethyl thiuram disulfide by the oxidation of a salt of dimethyl dithiocarbamic acid, the process comprising introducing said salt and a mineral acid separately and progressively into an aqueous solution of a salt of nitrous acid and a saturated aliphatic monohydric alcohol having less than 5 carbon atoms, the respective rates of introduction of said mineral acid and of said first-mentioned salt being regulated with respect to each other such as to maintain in the reaction mixture an unreacted portion of said first-mentioned salt until such time as the introduction of said first-mentioned salt is discontinued.

10. The process of claim 8 in which the first-

mentioned salt is the sodium salt of diethyl dithiocarbamic acid, in which the mineral acid is hydrogen chloride, and in which the salt of nitrous acid is sodium nitrite.

11. The process of claim 9 in which the mineral acid is hydrogen chloride, and in which the salt of nitrous acid is sodium nitrite.

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REFERENCES CITED

The following references are of record in the file of this patent:

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Number	Name	Date
1,908,935	Tschunkur	May 16, 1933
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Cambron, et al., "Canadian Journal of Research," vol. 2, page 151. (Copy in Scientific Library.)