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PRODUCTION OF FORMALDEHYDE FROM TRITHIANE

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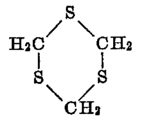
This invention relates to a process for the production of formaldehyde from trithiane, and more particularly, the invention is directed to an effective and economical method of converting trithiane into formaldehyde by reaction with readily available and inexpensive substances.

Trithiane is a cyclic trimeric thioformaldehyde of the formula



and can be prepared in a known manner by reacting commercial formaldehyde with hydrogen sulfide gas in an acid solution, e.g. hydrochloric acid. (See, for example, the disclosure by Bost and Constable in "Organic Syntheses," vol. 16, pp. 81–83 (1936).) It is also known that trithiane accumulates as a precipitate during the spinning of viscose rayon where the acid spin bath contains formaldehyde. Rather than simply discarding this trithiane by-product in a wasteful manner, it would be desirable to work up the spin bath by separating the precipitated trithiane and then converting it into a useful product, especially a product such as formaldehyde which could against be used for spinning viscose filaments in the production of rayon.

It is known that formaldehyde can be produced from trithiane by reacting the trithiane with silver sulfate and calcium oxide in the presence of oxygen or air at elevated temperatures. This process is very expensive, particularly due to the high price of the silver compound but also because silver sulfide is formed in the reaction with trithiane and it is possible to recover silver sulfate therefrom only with considerable difficulty, i.e. by using several reaction stages for the conversion of the silver sulfide into silver sulfate. This known process therefore has no practical significance or commercial advantage, especially in those cases in which the trithiane merely accrues as an undesirable by-product and must be transformed into formaldehyde in an economically productive manner. Furthermore, the known process gives relatively low yields of formaldehyde, even when carefully regenerating silver sulfate from the silver sulfide reaction product.

One object of the present invention is to provide a process for the production of formaldehyde from trithiane which can be carried out to obtain good yields in a relatively economical manner.

Another object of the invention is to provide a process for the regeneration of formaldehyde from trithiane initially obtained as a precipitate in the spinning bath used for the production of viscose rayon filaments.

Still another object of the invention is to provide a continuous method of converting trithiane into formaldehyde by reaction with substances which are relatively inexpensive and/or easily regenerated for reuse in the process.

These and other objects and advantages of the invention will become more apparent upon consideration of the following detailed description.

It has been found, in accordance with the present invention, that very practical results can be achieved in the production of formaldehyde from trithiane by contacting the trithiane with CuO and air, preferably with air or a similar oxygen-containing gas in admixture with steam, at a temperature between about 190° C. and 250° C. and condensing formaldehyde from the effluent gaseous reaction product. The process is preferably carried out at a temperature between about 210° C. and 235° C., and although the pressure is not a critical factor, the reaction is most conveniently carried out at approximately atmospheric pressure, i.e. normal pressure of about one atmosphere.

The copper-II-oxide (CuO) is introduced for intimate contact with the trithiane in accordance with the invention as a finely divided or pulverulent material or else it can be precipitated or applied onto an inert carrier such as aluminum oxide. While the amount of the copper-II-oxide can vary over a broad range, e.g. in a weight ratio of CuO to trithiane of about 1:1 to 6:1, it is preferable to employ the copper-II-oxide in a slight excess over that which would be theoretically required if all of the oxygen in this copper-oxide were substituted for the sulfur of the trithiane. Thus, the preferred ratio by weight of CuO to trithiane is about 2:1 to 4:1. This ratio by weight is taken with reference to the initial materials since at least part of the CuO is converted into CuS during the course of the reaction. Although it would be possible to use a much larger excess of CuO, it will be apparent that this would not ordinarily be economical.

The reaction time is not critical, but it is dependent upon the reaction temperature and the extent to which the CuO and trithiane are brought into intimate contact with each other and with the oxygen-containing gas such as air. Thus, the reaction proceeds most rapidly at higher temperatures and under conditions assuring the most intimate contact of the reactant materials. It is therefore preferable to work with a CuO-trithiane reaction mixture which is extended into a relatively thin layer of material in the reaction zone, e.g. by channeling the trithiane through a reaction zone packed with a carrier supported copper-II-oxide or by conducting an intimate mixture of the trithiane and copper-II-oxide in a relatively thin layer through the reaction zone. However, relatively good results are also achieved without providing a small layer thickness and without thorough mixing. For example, about two hours have been required for completion of the reaction in tests in which the CuO-trithiane mixture is simply placed in a reaction vessel and the reaction is carried out at a temperature of 190° C. without substantial mixing of the reactant materials. By comparison, when working with a smaller layer thickness or more intimate contact of the reactants and with better mixing and more rapid and thorough heating, then the reaction time at 230° C. can be reduced to a period of about two minutes.

It is generally necessary to carry out the reaction within the prescribed temperature range of 190 to 250° C., optimum results being achieved within the range of about 210 to 235° C. At temperatures below 190° C., an excessively long period of time is required to complete the reaction, while at temperatures over 250° C. the formaldehyde product is further oxidized so rapidly as to cause a decrease in yield. The retention time of the formaldehyde product in the reaction zone also influences the extent to which the formaldehyde is oxidized into formic acid and other secondary by-products. Therefore, some care must be exercised in order to avoid excessive oxidation of the desired formaldehyde product. Nevertheless, when working within the scope of the invention, the most favorable conditions can be readily determined by simple preliminary tests. The formaldehyde product can be obtained by the process according to the invention in yields of up to about 60%, with reference to the initial amount of trithiane induced into the reaction.

It is especially advantageous to carry out the reaction in a continuous operation wherein the copper-II-oxide and trithiane are conducted continuously through the reaction zone and maintained in intimate contact with each other and with a stream of air or a mixture of air and steam. For example, one can utilize the working principle of a single screw conveyor consisting of a double jacketed tube equipped with a screw or worm to convey the reactant materials therethrough. This jacketed tube is heated along its entire length by means of a suitable fluid heat-exchange medium, thereby assuring a constant temperature in the reaction zone. The copper-II-oxide and trithiane are initially mixed nad introduced into the reaction tube by means of a conventional feeding or dosing device, and the mixing of these materials is further promoted in the reaction tube by the screw conveyor. The retention time of the reaction mixture can be regulated by controlling the number of revolutions of the worm or screw per unit time, i.e. by controlling the turning rate of the screw. The air or other oxygen-containing gas can be introduced into the screw conveyor for passage therethrough, and the formaldehyde product is then separated with the stream of air at the outlet end of the reaction zone and condensed by cooling the effluent gas stream, e.g. in an air-cooled condenser.

When the reaction is carried out in this tubular reactor equipped with a screw conveyor, both the copper-II-oxide and trithiane are carried concurrently with each other and it is also preferable to conduct the stream of air or other oxygen-containing gas in the same direction. However, it is also possible to conduct the trithiane[1] in countercurrent flow to the copper-II-oxide, particularly where the latter is supported on an inert carrier substance such as aluminum oxide. In this case, the carrier supported CuO can flow continuously in one direction through the reaction zone while the trithiane is carried by the stream of air or similar oxygen-containing gas in the opposite direction. A CuO-CuS mixture is then removed from one end of the reaction zone and the formaldehyde is removed and condensed from the effluent gas at the other end of the reaction zone.

Regardless of the exact manner in which the process of the invention is carried out, the CuO-CuS mixture which is obtained after completion of the reaction can be very easily treated in order to regenerate CuO which can then be used again for further reaction with fresh trithiane. This regenerating treatment is merely a simple roasting of a copper sulfide in the mixture so that it is converted by oxidation back into CuO. This roasting can be carried out in situ after the reaction with trithiane is completed, or where the process is carried out continuously, the CuO-CuS mixture can be concurrently roasted in a separate continuous reaction stage and then recycled for use in the conversion of trithiane into formaldehyde. It is a particular advantage of the invention that the copper-II-oxide can be reused many times in this manner without any substantial reduction of the formaldehyde yield. In addition, the roasting of the copper sulfide for conversion into copper-II-oxide is a very well known single step reaction which is relatively inexpensive and which permits one to avoid a multi-stage regeneration of a metal salt.

The process of the invention is further illustrated by the following examples, but it will be understood that the invention is not limited to these examples.

Example 1

5 grams of trithiane are finely ground with 10 grams of CuO and heated for a period of 2 hours in a 250 ml. two-necked flask while passing air through the flask at a temperature of 190–200° C. The effluent gas stream is passed through an attached cooling tube in which there are separated 1.47 grams of paraformaldehyde. This corresponds to a yield of 45%.

Example 2

5 grams of trithiane are thoroughly mixed with 15 grams of CuO and heated for a period of one hour in a flask as in Example 1 with passage of air therethrough at 230° C. In the cooling tube, 1.65 grams of paraformaldehyde are separated, corresopnding to a yield of 51%.

Example 3

2 grams of trithiane are forced with a strong air stream containing steam over a packing or filling arranged in a reaction tube consisting of 7 grams of CuO on a carrier of 35 grams of Al_2O_3, which is maintained at a temperature of 220° C. The steam is preheated to 210° C. and introduced at the rate of 275 grams/hour in admixture with 60 liters/hour of air. A condensate is separated at the outlet end of the tube which contains 0.73 gram of formaldehyde. With reference to the initial 2 grams of trithiane, the resulting yield is 56%.

Example 4

1 part by weight of trithiane is finely ground with 3 parts by weight of CuO and led into a reaction tube heated by indirect heat exchange to 230° C. The reaction mixture is moved continuosly forward in the tube by means of a screw conveyor. The number of revolutions of the screw is determined in such a manner that the average retention time of the reaction mass in the heated tube amounts to about two minutes. At the same time, a stream of air preheated to 230° C. is led into the tube for concurrent flow and contact with the reaction mixture. At the discharge end of the reaction tube, the paraformaldehyde is removed with the air and is condensed and collected in an air cooler. The yield amounts to 60% with reference to the initial trithiane.

The resulting CuS-CuO mixture removed at the discharge end of the tube is converted back into CuO through a simple roasting, and can then reintroduced with fresh trithiane. In the reutilization of this regenerated CuO in the above described apparatus, a yield of 56% formaldehyde is obtained.

COMPARATIVE EXAMPLE

1 part by weight of trithiane is intimately mixed with 2 parts by weight of Ag_2SO_4 and 1 part by weight of CaO, and is conveyed with mixing through a reaction tube heated to 230° C. as described in Example 4. The yield of paraformaldehyde amounts to 33%.

If one attempts to regenerate the Ag_2SO_4/CaO-mixture from the discharged solids in the same manner as described in Example 4, i.e. by a simple roasting step, then in the reutilization of the roasted product, there is obtained a yield of only about 3.6% formaldehyde. In order to achieve about the same yield of formaldehyde as described above, i.e. 33%, the silver catalyst must be converted back into Ag_2SO_4 after thoroughly roasting the sulfur in known manner, i.e. by further treatment with sulfuric acid and evaporation.

It will be apparent from the foregoing examples that the process of the present invention not only permits a substantial increase in the yield of formaldehyde but also avoids a costly and difficult regeneration of the metal catalyst. The formaldehyde product is obtained from the process in the form of a good commercial grade of paraformaldehyde and can therefore be used directly in the spinning bath for the production of viscose rayon filaments. Furthermore, the process of the invention can be

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[1] In gaseous form.

readily adapted to continuous operation, including the regeneration of the copper oxide from copper sulfide formed during the reaction. For these reasons, the novel process of the invention is quite suitable for commercial exploitation, and variations or modifications of the process can be readily made by one skilled in this art without departing from the spirit or scope of the invention as claimed hereinbelow.

The invention is hereby claimed as follows:

1. A process for the production of formaldehyde from trithiane which comprises contacting said trithiane with CuO and air at a temperature between about 190° C. and 250° C. and condensing formaldehyde from the effluent gaseous reaction product.

2. A process as claimed in claim **1** wherein said temperature is between about 210° C. and 230° C.

3. A process as claimed in claim **1** wherein said air is admixed with steam for contact with said trithiane.

4. A process as claimed in claim **1** wherein the ratio by weight of CuO to trithiane is about 1:1 to 6:1.

5. A process as claimed in claim **1** wherein said CuO is deposited on an inert carrier.

6. A process as claimed in claim **1** wherein a mixture of trithiane and CuO is conducted continuously through a reaction zone maintained at a temperature between about 190° C. and 250° C. together with a preheated stream of air.

7. A process as claimed in claim **6** wherein said reaction zone is maintained at a temperature between about 210° C. and 230° C.

8. A process as claimed in claim **6** wherein said stream of air is admixed with steam.

9. A process as claimed in claim **6** wherein the ratio by weight of CuO to trithiane in said mixture is about 2:1 to 4:1.

10. A process as claimed in claim **6** wherein said CuO is at least partly converted into CuS in said reaction zone, said CuS together with unreacted CuO is continuously removed from the reaction zone and then oxidized to reform CuO, and trithiane is again continuously conducted through said reaction zone in admixture with said reformed CuO and air.

References Cited

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