United States Patent Office 3,046,289 Patented July 24, 1962

3,046,289

REAGENTS DERIVED FROM DITHIOL

Robert E. D. Clark, Cambridge, England, assignor to Fisher Scientific Company, Pittsburgh, Pa.

No Drawing. Filed Oct. 3, 1960, Ser. No. 59,775
Claims priority, application Great Britain Mar. 20, 1957
1 Claim. (Cl. 260—429.9)

This invention relates to improved reagents derived from dithiol. It relates particularly to zinc derivatives of toluene-3,4-dithiol, i.e., to zinc toluene-3,4-dithiol and to certain adducts thereof.

The present application is a continuation-in-part of my application Serial No. 709,447, filed January 17, 1958, and now abandoned.

Toluene-3,4-dithiol, hereinafter referred to as "dithiol," was first described in 1936 (W. H. Mills and R. E. D. Clark, Journal of Chemical Society, 1936, pp. 175–181). Shortly after (Analyst, 1936, vol. 61, pp. 242–245), I drew attention to the fact that this and certain other compounds of the aromatic ortho-dimercaptan class afford a specific and highly sensitive reagent for the element tin and that they give rise to colored derivatives (mercaptides) with many heavy metals.

Despite two decades of widespread use, however, no attention has been drawn to many of the valuable properties of this class of reagent. Most of its specific or highly selective reactions with cations and its other desirable properties have remained undiscovered. As a result, dithiol, the only member of the class to be made commercially, has remained a little known product sold in small quantities only and at a high price.

These facts must be ascribed chiefly to the difficulties hitherto associated with the use and storage of dithiol.

Since the beginning of its commercial manufacture in 1936 or soon afterwards, dithiol has been marketed in sealed ampoules since it keeps badly when exposed to air. Its solutions, especially those in alkali, are even more unstable to air than free dithiol and must usually be kept in a refrigerator or even under hydrogen. The original suggestion that, after dissolution, the reagent should be stored in the presence of an excess of thioglycollic acid, has often been adopted. Nevertheless, the solutions are not very stable whilst the presence of thioglycollic acid is rarely desirable.

The widespread use of thioglycollic acid has, in fact, obscured many reactions in an acid and all reactions in an alkaline medium—especially those with copper, cobalt, iron and vanadium. In an acid solution, moreover, the difficulty of obtaining dithiol in complete absence of the disulphide, its oxidation product, has also obscured its highly selective reactions with arsenic and germanium.

According to the prevent invention, the difficulties associated with the storage of dithiol are overcome by preparing a zinc derivative of dithiol. The zinc derivative of dithiol can be converted into dithiol shortly before use, or may in some instances be used without such conversion.

Zinc toluene-3,4-dithiol, possessing the structural formula $CH_3.C_6H_3.S_2Zn$, hereinafter referred to as "zinc dithiol," can be stored in ordinary containers for long periods of time with little or no decomposition and yet free dithiol can be regenerated at will from it within 15–30 seconds. Zinc dithiol is odorless, colorless, is readily soluble both in alkali and in aqueous-alcoholic hydrochloric acid, and it is readily prepared from commercially available materials which are free from metals which give colors with orthodimercaptobenzenes. The zinc of the zinc dithiol is easily replaced by many other metallic ions so that the zinc dithiol may usually be used directly in place of free dithiol.

Zinc dithiol readily gives adducts with bases. Thus,

zinc dithiols reacts with two molecules of pyridine or with one molecule of ethylenediamine. These adducts may often be obtained crystalline and they may usually be used in place of zinc dithiol as a source of dithiol.

By these preferred means, the dithiol is stored and rendered readily available as required.

Preparation of Zinc Dithiol

Zinc dithiol may be prepared by adding dithiol to zinc acetate solution. Unless the reaction is carried out on a very small scale, however, the bulky solid formed occludes much unreacted dithiol. After breaking up, this may later be removed by washing with a solvent, but unless this is performed in the absence of air, much dithiol is lost by oxidation.

The difficulty may be overcome in the following way. Excess (more than 1 mole) of pure zinc acetate for each mole of dithiol to be added is dissolved in hot water, at least 50 ml. of water being allowed for each gram of dithiol to be added. The vessel is fitted with an efficient reflux condenser and the dithiol dissolved in 5–10-fold excess of ethylene chloride or chloroform is added slowly to the briskly boiling liquid. The zinc salt separates in large masses. These are broken as far as possible and the mixture is refluxed vigorously for 2 hours, with addition of more solvent if desired. In this operation, the refluxing solvent serves to extract the solid. The mixture is filtered and the white, nearly pure, very bulky precipitate, now completely free from dithiol, is dried at 90°. If the zinc dithiol is required to be completely free from dithioldisulphide, it may be extracted with carbon disulphide, but this is not usually necessary. The yield is theoretical. Analysis indicates that the product has the empirical formula $C_7H_6S_2Zn$.

Preparation of Adducts of Zinc Dithiol with Bases

These adducts are easily prepared by dissolving zinc dithiol in an excess of the base and then adding a solvent miscible with the base until the adduct is precipitated. If the dilution is carried out hot, the adducts may crystallize on cooling.

For example, 1 gm. of zinc dithiol is dissolved in 10–15 ml. of hot pyridine. Hot water is then added slowly until a permanent precipitate just forms. The liquid is cooled and the crystalline adduct filtered off. The same method may be used for ethylenediamine for which, say, 5 ml. of ethylenediamine hydrate is sufficient.

No difficulties are experienced in this class of preparation and great latitude is permissible in formulating the precise conditions of formation.

Preparation of a Solution of Dithiol from Zinc Dithiol

A suitable quantity of zinc dithiol, say 50–200 mg., is shaken with 3–10 ml. of industrial alcohol and a few drops of concentrated hydrochloric acid are added. The zinc dithiol dissolves in a few seconds to give a clear, colorless solution of dithiol.

Solutions of dithiol so prepared contain zinc chloride. They, therefore, fail to give derivatives of dithiol with metals less reactive than zinc towards dithiol, except that the reaction with iron is obtained though with reduced intensity. However, zinc dithiol may also be used to give dithiol free from inorganic compounds.

Preparation, from Zinc Dithiol, of a Solution of Dithiol Free from Inorganic Compounds

A little sodium hypophosphite, say 50 mg., is added to a suitable volume, say 5 ml., of, say, 2 normal sulphuric acid in order to insure reducing conditions. The required quantity, say 50–200 mg., of zinc dithiol is added and, after warming to decompose the zinc salt, the oily dithiol is extracted with, say, 2 ml. of a heavy organic solvent such

as ethylene chloride or chloroform. There is no tendency for an emulsion to form. The lower layer containing the dithiol free from inorganic compounds and oxidation products, is separated and used as desired. For many purposes, it is convenient to dilute it with alcohol.

Preparation from Zinc Dithiol, of a Solution of the Sodium Salt of Dithiol

Zinc dithiol may be added directly to dilute sodium hydroxide solution, 2 normal being suitable, when it dissolves to give the sodium salt of dithiol. This solution rapidly gives a precipitation in air.

Determination of the Strength of Any of the Above Dithiol Solutions

The solution of dithiol, the strength of which is to be determined, is placed in a burette and is added dropwise to a known volume of .01 molar mercuric chloride solution mixed with an equal volume of pyridine. If a drop of .01 molar cobalt chloride is added, a blue color appears suddenly when the end point is reached. Since one molecule of dithiol reacts with one atom of mercury, the strength of the dithiol solution is easily ascertained. Having determined the strength of the dithiol solution, a standard dithiol solution, conveniently of .01 to .05 molar strength, can readily be made from it.

Uses of Zinc Dithiol

Zinc dithiol can be used to test ores, often in complex combinations, under field conditions with few chemical reagents and no apparatus other than test tubes, a teat pipette, a glass slide and a source of heat, in a total time which rarely exceeds one minute. A few of these tests together with an indication of the main principles and procedures are as follows:

Copper.—A trace of the ore, placed on a glass slide, is treated with a drop of 2 normal sodium hydroxide and a little zinc dithiol. In the presence of copper the solution rapidly becomes orange with non-sulphidic ores in the cold, with sulphuidic ores, on warming.

Iron and cobalt.—As for copper, but a drop of pyridine is used instead of sodium hydroxide. Cobalt gives a blue color and iron a red. On gently taking to dryness, patches of the separate colors and of green (copper) may be seen when more than one of the metals is present. Powdered zinc dithiol placed on an ore and moistened with pyridine often imparts strong colors to ores containing copper, iron and cobalt, the separate colors appearing as patches. This method is particularly useful in testing for cobalt.

Tin.—A few milligrams of the ore are heated for 30 seconds with a pellet of potassium hydroxide and a drop of water. On adding 2 normal hydrochloric acid and zinc dithiol, a red precipitate is immediately obtained.

In other cases the coarsely powdered ore may be partly dissolved by boiling for 30 seconds with hydrochloric acid with or without the addition of a crystal of potassium chlorate, or it may be heated for a like period with dry barium nitrate and barium peroxide and the hot tube containing the mixture dropped into concentrated hydrochloric acid placed in a larger tube. To the solution obtained in one of these ways, zinc dithiol is added, and if necessary, the acid mixture is diluted. In this way characteristic prepicitates are at once obtained with molybdenum, gold, platinum, mercury, antimony, tungsten, bismuth and other elements.

In testing for arsenic the solution of ore in 3–4 normal hydrochloric acid is warmed with a crystal of sodium hypophosphite and zinc dithiol is added when the solution becomes turbid and the turbidity is stable to boiling. In this simple form the test is not specific but zinc dithiol itself will often indicate when interfering elements are present. Thus the appearance of a yellow oil on the surface of the liquid indicates antimony which is the only more common element to interfere; but its interference is stopped if a little copper powder is added in the original test. Antimony (v) gives a brilliant red color in pyridine-hydrochloric acid mixture in the presence of dithiol. Vanadium gives a brilliant sea green color in the presence of pyridine. Many other tests also are available and in practically all instances the reactions are highly sensitive and highly selective or specific.

It is thought that the details of the invention will have been clearly understood from the foregoing description. Minor changes may be resorted to without departing from the spirit of the invention, wherefor it is my intention that no limitation be implied and that the hereto annexed claim be given a scope fully commensurate with the broadest interpretation to which the employed language admits.

I claim:

Zinc toluene-3,4-dithiol having the empirical formula $C_7H_6S_2Zn$.

References Cited in the file of this patent

Krebs et al.: Z. anorg. u. allgem. Chem., vol. 276, p. 140 (1954).