at room temperature until the solution remained slightly milky. It was then allowed to stand with occasional agitation and scratching of the walls until crystallization started. Once seed crystals were obtained subsequent recrystallizations were comparatively easy.

N^4-Sulfanilyldisulfanilamide.—One-half mole of sulfanilamide was dissolved in 500 cc. of water with sufficient sodium hydroxide to give a *p*H of 10–12; 1.2 moles of freshly prepared N-acetylsulfanilyl chloride was added over half an hour at 35–40° while maintaining the above *p*H by addition of 50% sodium hydroxide as necessary. Stirring was continued for one hour, then 100 g. of sodium hydroxide was added, and the mixture boiled for two hours. The hydrolysis mixture was neutralized with concentrated hydrochloric acid, cooled, crystals of crude N^1-sodium-N^4-sulfanilyldisulfanilamide filtered off, and recrystallized several times from water, using activated charcoal. The free amide was made by acidification of a solution of the sodium salt. The initial amorphous mass was crystallized by rubbing in alcohol.

N^1,N^4,N$^{4'}$-Trisodium N^4,N$^{4'}$-disulfanilyldisulfanilamide.—This was made by the general procedure starting with an equivalent of N^1-sodium disulfanilamide. Attempts to prepare a crystalline monosodium salt or crystalline free amide failed. The trisodium salt (actually a mixture with some of the disodium salt) was crystallized from a concentrated aqueous solution at *p*H 9–10, by dilution with alcohol.

N^1-(2-Hydroxyethyl)-N^3-metanilylmetanilamide.—One-third mole of N^1-(2-hydroxyethyl)-metanilamide was dissolved in 300 cc. of water containing 30 g. of boric acid; $^1/_3$ mole of *m*-nitrobenzenesulfonyl chloride was added over an hour at 55–65° with vigorous agitation while maintaining a *p*H of 6–8 by addition of 50% sodium hydroxide solution as required. The nitro compound which separated on cooling was reduced with 150 g. of fine iron, 500 cc. of water, and 1 cc. of glacial acetic acid at 95–100°. After complete reduction excess sodium hydroxide was added to dissolve completely the product, the mixture was filtered, and the filtrate neutralized. A sticky mass separated which crystallized on standing overnight. This crude product was recrystallized by dissolving in hot alcohol, treating with activated charcoal, then diluting gradually with water, cooling and seeding. After several recrystallizations, colorless crystals were obtained.

Boric acid was used in the hope that by forming a complex with the hydroxyl groups, it would aid in preventing formation of sulfonic esters. Success in obtaining a crystalline product through its use, where previously there had been failure, leads us to believe that it was of value.

Summary

A series of *strepto*-N-polysulfanilyl derivatives of aminobenzenesulfonic acids and carboxylic acids, hydroxyalkylamines, sulfonamides, and disulfonamides are described, together with preliminary results of the pharmacological study of their effect in mice infected with *β*-hemolytic streptococci.

No general conclusions can be drawn concerning the effect of increasing the number of sulfanilyl groups.

Better activity was shown by N^3-sulfanilylmetanilamide than by N^4-metanilylsulfanilamide. This was predicted from previous results.

Certain of these compounds appear effective in virus diseases, but caution is expressed against assuming that the results of these preliminary studies in mice are translatable to human therapy.

BOUND BROOK, N. J. RECEIVED APRIL 27, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN]

Ethylenediamine and Propylenediamine Vanadates

BY EUGENE H. HUFFMAN

In the course of an investigation, some diamine vanadates were desired. A search of the literature did not reveal the previous preparation of these, though some alkyl amine vanadates[1] and a pyridinium vanadate[2] have been described. This paper describes the preparation and some properties of hydrated hexavanadates of ethylenediamine and propylenediamine and the metavanadate of ethylenediamine.

Preparation

Ethylenediamine and Propylenediamine Hexavanadates.—Ten grams of vanadium pentoxide (either C. P. grade or prepared by gently heating ammonium metavanadate) is added to a solution of 5 cc. of 69.8% ethylenediamine and 15 cc. of water, or 8 g. of vanadium pentoxide to 5 cc. of 70–75% propylenediamine and 15 cc. of water. Then 15 cc. of 30% hydrogen peroxide is added slowly, with stirring, over a period of half an hour, while keeping the temperature below 60°. The mixture is filtered, washed with 25 cc. of water, to which is added 3 cc. of 30% hydrogen peroxide, and the filtrate and washings diluted to 150 cc. After just neutralizing the solution to

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[1] Bailey, *J. Chem. Soc.*, **45**, 690 (1884); *Compt. rend.*, **104**, 1844 (1887).

[2] Katzoff and Roseman, THIS JOURNAL, **58**, 1785 (1936).

litmus with the corresponding diamine, crystallization usually begins in thirty minutes. It can be hastened by the addition of a small amount of the diamine dihydrochloride. The bright brownish-yellow product is filtered off, washed with water, and air-dried at room temperature.

Ethylenediamine Metavanadate.—This compound may be prepared by the following three methods. (1) Solid ethylenediamine dihydrochloride is added slowly to a saturated solution of ammonium metavanadate (prepared by heating to boiling, cooling, and filtering) until precipitation is complete. About 3 g. of the hydrochloride is required for every 100 cc. of saturated metavanadate solution. The golden-yellow product is washed on a filter with water until free from chloride and dried over calcium chloride.

(2) Three grams of vanadium pentoxide is added to a mixture of 5 cc. of ethylenediamine (69.8%) and 10 cc. of water. The mixture is heated to 90° for five minutes, filtered, and cooled to 20°. The brown turbid appearance is discharged by adding 2 drops of 30% hydrogen peroxide and allowing to stand for ten minutes. The vanadate is precipitated either by diluting to 200 cc. and passing carbon dioxide into the solution or by diluting to 40 cc. and slowly adding, with stirring, 150 cc. of 95% ethyl alcohol. The white product is washed first with four 10-cc. portions of alcohol to remove excess amine, and then with water to remove carbonate. If it is washed with water before the amine is removed, the precipitate redissolves.

(3) Two grams of the hexavanadate is dissolved in 6 cc. of ethylenediamine (69.8%) and 30 cc. of water. The orange color of the solution changes to colorless in forty minutes. The solution is diluted to 50 cc. and 100 cc. of 95% ethyl alcohol added, with stirring, to precipitate the white metavanadate. The product is filtered, washed with four 10-cc. portions of alcohol and then with water.

Similar attempts to prepare propylenediamine metavanadate gave discordant results which approached the hexavanadate in composition.

Analysis

The compounds were analyzed for vanadium and diamine. (1) Vanadium is determined readily by direct ignition to vanadium pentoxide in a platinum crucible. The fluid vanadium pentoxide should be allowed to run off the un-oxidized part to ensure complete oxidation.

(2) The diamine can be determined by a modified Kjeldahl method. A sample (0.4 to 0.6 g.) is digested with sulfuric acid and potassium sulfate, but without the addition of any other oxidation catalyst. The vanadium pentoxide brings about complete oxidation in one and a quarter hours. The ammonia is then distilled and titrated in the usual manner. The results[3] allow the ratio between vanadium and diamine to be determined quite accurately.

The water content was based upon the vanadium and diamine determinations. The results were: (1) ethylenediamine metavanadate, 38.99, 38.99, 39.08, and 39.13% vanadium and 23.24, 23.02, 23.73, and 22.90% ethylenediamine; calculated for $C_2H_4(NH_2)_2 \cdot 2HVO_3$, 39.19% vanadium and 23.11% ethylenediamine; (2) ethylenediamine hexavanadate, 39.46 and 39.50% vanadium and 15.31 and 15.25% ethylenediamine; calculated for $2C_2H_4(NH_2)_2 \cdot H_4V_6O_{17} \cdot 4H_2O$, 39.50% vanadium and 15.53% propylenediamine; (3) propylenediamine hexavanadate, 39.75, 39.99, and 40.10% vanadium and 19.56 and 19.20% propylenediamine; calculated for $2C_3H_6(NH_2)_2 \cdot H_4V_6O_{17} \cdot 2H_2O$, 39.91% vanadium and 19.35% propylenediamine.

Properties

Ethylenediamine metavanadate is golden-yellow in color when prepared by precipitation from an ammonium metavanadate solution or white when precipitated from an ethylenediamine solution. Both hexavanadates are brownish-yellow. All three compounds are insoluble in alcohol, ether, acetone, dioxane, and benzene, and are not appreciably soluble in water. All are soluble in aqueous solutions of ammonia, ethylenediamine, propylenediamine, and 30% hydrogen peroxide.

The compounds undergo no detectable change in composition on standing in diffused light for one month, but turn dark when exposed to direct sunlight. The hexavanadate and yellow metavanadate of ethylenediamine change to the white metavanadate when allowed to remain in a solution of ethylenediamine until just colorless.

Summary

The preparation and some properties of ethylenediamine hexavanadate, propylenediamine hexavanadate, and ethylenediamine metavanadate have been described. Attempts to prepare propylenediamine metavanadate gave discordant results.

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[3] The method was checked by determining the diamine content of ethylenediamine dihydrochloride, carefully purified by recrystallization and dried over calcium chloride. For this purpose about 0.2 g. of vanadium pentoxide was used as a catalyst in the digestion. The variation amounts to 0.5 to 0.8% of the diamine content.