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METHOD OF PREPARING SULFAMIC ACIDS FROM ORGANIC ISOCYANATES

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The present invention relates to a method of preparing sulfamic acids from organic isocyanates and, more particularly, it relates to a method of preparing sulfamic acids by reacting organic isocyanates with sulfuric acid or oleum.

I have found that if organic isocyanates of the general formula (R')NCO or OCN(R'')NCO, where R' is any alkyl radical and R'' is any bivalent aliphatic hydrocarbon radical that are not readily sulfonated, sulfated or oxidized under the reaction conditions, are treated with sulfuric acid or oleum, the corresponding sulfamic and di-sulfamic acids will be produced in very satisfactory yield.

Accordingly, it is an object of the present invention to provide a method of preparing mono- and di-sulfamic acids from corresponding organic mono- and di-isocyanates.

Another object of the present invention is to provide a novel di-sulfamic acid of a type never produced heretofore.

Other objects and advantages of the present invention will become more apparent as it is described in detail below.

The novel process that I have discovered for forming the mono- and di-sulfamic acids may be generally represented by the following reaction

$$W(NCO)_z + (H_2SO_4)_z = W(NHSO_3H)_z + (CO_2)_z$$

where W is R' when z is equal to 1 and W is R'' when z is equal to 2, and where R' and R'' are alkyl and bivalent aliphatic hydrocarbon radicals, respectively, that are not readily sulfonated, sulfated, or oxidized under the reaction conditions.

With respect to the process for forming the mono-sulfamic acids, it may be represented by the following equation

$$R'NCO + H_2SO_4 = R'NHSO_3H + CO_2$$

where R' is any alkyl radical that is not readily sulfonated, sulfated or oxidized under the conditions of the reaction.

The process for forming the di-sulfamic acid may be represented by the equation

$$OCNR''NCO + 2H_2SO_4 = HO_3SNHR''HNSO_3H + 2CO_2$$

where R'' is any bivalent aliphatic hydrocarbon radical that is not readily sulfonated, sulfated or oxidized under the conditions of the process.

I have discovered that any sulfonation, sulfation or oxidation of the alkyl or bivalent aliphatic hydrocarbon groups that may occur may be completely eliminated or at least reduced to a minimum amount, if the process is carried out at the lowest temperature at which the evolution of carbon dioxide occurs. To effect this, the process may be performed in an ice cooled vessel. However, higher temperatures may be employed where the alkyl or bivalent aliphatic hydrocarbon groups are particularly insensitive to sulfonation, sulfation or oxidation.

Although the above reactions may be carried out with 100% sulfuric acid, I prefer to employ oleum for the sake

of convenience. Additionally, I prefer an oleum with a low sulfur trioxide content rather than one with a high sulfur trioxide content because the sulfonating, sulfating and oxidizing ability of oleum increases with an increase in sulfur trioxide content. Thus the possibility of undesired attack on the alkyl or bivalent aliphatic hydrocarbon group is reduced by using an oleum of low sulfur trioxide content.

Concentrated sulfuric acid may also be employed for the above reactions but it is noted that amine bisulfates are formed along with the sulfamic acids. This is due to hydrolysis of the organic isocyanates by the water contained in the concentrated sulfuric acid. Thus, it is preferable to use 100% sulfuric acid or oleum if sulfamic acids are to be obtained in high yields.

In order to isolate the sulfamic acids produced by my process, I dilute the reaction mixture with a liquid in which the sulfamic acid is insoluble and in which the excess sulfuric acid or oleum is readily soluble. Ether is such a liquid which I have found useful for this purpose. I then filter the ether mixture to obtain the crystalline sulfamic acid.

Although the above ether filtration technique leaves the sulfamic acid in a pure form, it may be necessary in some cases to recrystallize the sulfamic acids formed from a suitable solvent or solvent mixture. If this recrystallization still does not suffice to obtain the sulfamic acids in pure form, I employ the use of lead oxide to purify the product.

The lead oxide method comprises the steps of adding lead oxide to an aqueous solution of the sulfamic acid to be purified. Lead hydroxide and lead sulfate are filtered out of the solution. The filtered solution containing the water soluble lead salt of the sulfamic acid is treated with hydrogen sulfide to precipitate lead sulfide. The lead sulfide is then removed by filtration. Next, the filtrate is preferably evaporated at reduced pressure and temperature (less than 100° C.) to avoid hydrolysis of the sulfamic acid. The remaining material will be pure crystals of the sulfamic acid.

Below are several examples which illustrate my invention but do not in any way limit it thereto.

Example I

To prepare ethyl sulfamic acid, 6.0 g. of ethyl isocyanate were added dropwise to 70 g. of ice cooled and mechanically stirred 20% oleum. The reaction proceeded with the evolution of carbon dioxide. A white solid, which dissolved with bubbling, was noticed during the reaction. When one half of the isocyanate had been added, the ice bath was removed and the reaction continued. After all the isocyanate was added, the reaction mixture was slightly lukewarm.

The chilled reaction mixture was poured slowly into 450 ml. of chilled anhydrous ether, which mixture was ice cooled and shaken during the mixing. The precipitated ethyl sulfamic acid was collected on a sintered-glass funnel and washed with ether. The ethyl sulfamic acid weighed 8.8 g. which represented an 83% yield. Also, it gave only a very faint test for sulfate ion.

To purify the product, it was dissolved in methanol and reprecipitated by the addition of a relatively large quantity of ether.

Example II

The ethyl sulfamic acid formed in Example I was dissolved in water. More than an equivalent amount of lead monoxide was added to the solution. Excess lead hydroxide and lead sulfate were removed by filtration. The filtrate, which contained lead ethylsulfamate, was treated with hydrogen sulfide to precipitate lead sulfide. After filtration to remove the lead sulfide, the filtrate was distilled at reduced pressure. The distilling bath did not exceed 55° C. The residual solid was dissolved in methanol and, on slow evaporation of the solvent, large crystals of ethyl sulfamic acid were obtained. These crystals had a melting point of 170–171° C.

This example of the lead oxide purification method need only be employed when there is heavy sulfate contamination of the sulfamic acid produced in accord with my invention. In the case of the sulfamic acid produced in Example I, it was not actually necessary. However, this example is given as an illustration of the lead oxide method.

Example III

In order to form hexamethylenedisulfamic acid, 5.3 g. of hexamethylene di-isocyanate were slowly added to 22.4 g. of ice cooled and mechanically stirred 5% oleum. It was noted that a white solid formed and carbon dioxide was evolved. After all the isocyanate was added to the reaction mixture, gas evolution continued sluggishly in the cold. In order to carry the reaction to completion, the mixture was gradually heated to 95° C., at which time no more gas was given off. It is possible that the second isocyanate group requires a higher reaction temperature because of the low solubility of the substance formed in the intermediate stage.

The reaction mixture, which contained a finely divided solid, was chilled to 0° C. whereupon considerably more solid material was precipitated. The chilled mixture was added to 300 ml. of ice cooled ether and filtered by suction. The filtered hexamethylenedisulfamic acid was washed with ether. It was found to weigh 8.6 g., which was 98.9% of theoretical yield.

Complete removal of sulfate ion was not achieved even though the product was dissolved in methanol and reprecipitated by ether. Accordingly, the lead oxide purification method described in Example II was employed to obtain sulfate free hexamethylenedisulfamic acid.

While the invention has been described in detail and shown with respect to the accompanying examples, it is not to be limited thereto, since many changes and modifications may be made in the invention without departing from the spirit and scope thereof. Hence, it is desired to cover any and all forms and modifications of the invention which may come within the language and scope of any one or more of the appended claims.

I claim:

1. A method of forming sulfamic acids which comprises mixing an alkyl isocyanate with a sulfonating agent which is at least about 100% H_2SO_4, and maintaining a temperature at which evolution of carbon dioxide occurs, whereby alkyl sulfamic acid is formed.

2. A method of forming sulfamic acids which comprises mixing an alkyl isocyanate wih a sulfonating agent which is at least about 100% H_2SO_4, and maintaining a temperature at which evolution of carbon dioxide occurs, whereby alkyl sulfamic acid is formed, then diluting the reaction mixture with a liquid in which said sulfamic acid is insoluble and said sulfuric acid is soluble and recovering said sulfamic acid.

3. A method of forming sulfamic acids which comprises introducing with stirring small amounts of an alkyl isocyanate into a body of a sulfonating agent which is at least about 100% H_2SO_4, and maintaining a temperature at which evolution of carbon dioxide occurs, whereby alkyl sulfamic acid is formed.

4. A method of forming sulfamic acids which comprises inmixing an alkyl isocyanate with a sulfonating agent which is at least about 100% H_2SO_4, and maintaining a temperature at which evolution of carbon dioxide occurs by cooling the reaction mixture below room temperature, whereby alkyl sulfamic acid is formed.

5. A method of forming sulfamic acids which comprises mixing an alkyl isocyanate with a sulfonating agent which is sulfuric acid containing excess SO_3, and maintaining a temperature at which evolution of carbon dioxide occurs, whereby alkyl sulfamic acid is formed.

6. A method according to claim 1 in which the isocyanate is a monoalkyl isocyanate.

7. A method according to claim 1 in which the isocyanate is an aliphatic di-isocyanate.

8. A method according to claim 1 in which the isocyanate is ethyl isocyanate.

9. A method according to claim 1 in which the isocyanate is hexamethylene di-isocyanate.

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