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PROCESSES FOR PRODUCTION OF PYRIDINE 3-SULPHONIC ACID AND ITS SALTS

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Our invention relates to improvements in the process of sulphonating pyridine and refers particularly in processes for obtaining pyridine 3-sulphonic acid and its salts.

While the sulphonation of many aromatic compounds of the benzene series is easily accomplished by treating them with concentrated sulphuric acid or oleum at relatively low temperatures, the yield being almost quantitative, pyridine and its derivatives offer considerable resistance to sulphonation by the processes adapted for the sulphonation of members of the benzene series.

Numerous attempts have been made to overcome the difficulties present in the sulphonation of pyridine, but they have all resulted in the use of excessive amounts of the sulphonating compound, prolonged heating at highly elevated temperatures and of comparatively small yields.

The following are among the previous attempts to sulphonate pyridine:

One process consisted in heating the pyridine with excessive proportions of sulphuric acid and sulphuric anhydride at 330°–350° C. for sixty hours, the sulphuric acid which was distilled off at these high temperatures being replaced from time to time. In addition to the large amounts of the sulphonating chemicals, and the length of time employed, the yields were very small.

Attempts have been made to produce the sulphonation by heating pyridine with concentrated sulphuric acid in sealed tubes to the boiling point of the mixture, 320°–330° C., for thirty or forty hours without satisfactory results.

Further attempts have been made by adding a catalyst, mercury sulphate, vanadium sulphate, aluminum sulphate or magnesium sulphate, to the pyridine, sulphuric acid and sulphuric anhydride, heating to 330°–350° C. for forty to sixty hours and replacing the distilled sulphuric acid with additional amounts of the acid. While this process increased the yield above that obtained in the absence of the catalyst, it still possessed the disadvantages of the former processes as regards the amounts of sulphonating materials employed.

Our invention presents processes for the production of pyridine 3-sulphonic acid in which the amount of chemicals and the time of procedure are materially decreased, and the yield is considerably increased over those of the described processes, these advantageous results being obtained by the particular steps of procedure of our processes which are not present in the prior processes.

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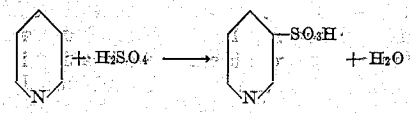
The sulphonation of pyridine takes place according to the following formula:



It is evident from this equation that each mol of pyridine (m. wt. 79) liberates one mol of water (18) during sulphonation.

We have found that this liberated water dilutes the sulphuric acid to such an extent as to make it too weak for the sulphonation to any considerable degree and that the presence of a dehydrating agent in sufficient quantity to take up the water results in increased yields. An ideal dehydrating agent for this purpose is fuming sulphuric acid, the SO_3 of which forms sulphuric acid with the water. Using an oleum containing 20% SO_3, five parts are required theoretically to take care of the produced water.

It must be considered, however, that when pyridine is added to the oleum, some of the SO_3 escapes from the oleum during the heating of the sulphonating process and, hence, increased yields are obtained by employing an amount in excess of the theoretical quantity.

We have now found, that we can increase the yield of pyridine 3-sulphonic acid considerably by adding oleum to the reaction mixture at intervals. We have found also that it is advisable to add a further small quantity of catalyst with each addition of oleum.

With periodical additions of oleum and proper catalysts we have practically doubled the yield of pyridine 3-sulphonic acid compared with yields obtained by the previously described methods. For instance, using mercury or its salts as catalysts, the yield is 37%, our yield is about 75%; using magnesium as catalyst by the usual method, the yield is 14%, by our method the yield is about 23%; using aluminum as catalyst by the usual method, the yield is 12%, our yield is about 22%.

An object of this invention, therefore, is to increase the yield of pyridine 3-sulphonic acid, while at the same time reducing the amount of the sulphonating agent and the time of operation.

Another object is to prevent the undue dilution of the sulphonating agent by the periodical addition of a dehydrating agent.

Further objects of this invention will be evident from the herein described processes and the results produced thereby.

Among the catalysts suitable for application in our processes are mercury, aluminum, magnesium and vanadium and their salts, but we do not limit ourselves to these catalytic metals, as other suitable catalytic metals may be employed. These catalysts dissolve in the hot sulphuric acid as the corresponding sulphates, and therefore, the sulphates may be added to the sulphonating mixture.

Our preferred method of sulphonation can be clearly seen from the following illustrative examples. All parts referred to in these examples are given by weights.

Example I

250 parts of pyridine are run as a fine stream into 750 parts of oleum (fuming sulphuric acid, 20% SO_3) under stirring and cooling, taking care that the temperature does not rise over 75° C. The mixture now consists of a solution of pyridinium sulphate in oleum. Three parts of mercury are added to the solution and heated to about 250°–270° C. under constant stirring. After an hour heating 160 parts of oleum and 1.5 parts of mercury are added. The heating is continued, and after the second and third hour heating, each time the same amount of mercury and oleum is added thereto. The heating is then continued for two more hours and then cooled down to room temperature. The mixture is now added to 7500 parts of water and neutralized with finely pulverized calcium carbonate.

The calcium sulphate formed is filtered off and washed with hot water. The filtrate now contains calcium 3-pyridine sulphonate and the unreacted pyridine, which pyridine may be recovered. Sodium or potassium carbonate is now added to the solution till it becomes alkaline to phenolphthalein, the calcium carbonate is filtered off and the solution is evaporated to dryness. By using 130 parts of sodium carbonate, 442 parts of sodium 3-pyridine sulphonate is obtained which represents 77% yield. If the free 3-pyridine sulphonic acid is required, the calcium is removed from the calcium salt by the addition of the theoretical amount of sulphuric acid, the calcium sulphate is filtered off, and the solution is evaporated to dryness.

Example II

A pyridinium sulphate solution in 50 parts oleum is prepared from 25 parts of pyridine as described in Example I. 1.5 parts of magnesium turnings are added to the solution and heated to 270°–300° C. After heating for one hour, 0.375 part of magnesium and 16 parts oleum are added. This is repeated after the second and third hour of heating, and then the heating is continued for nine more hours. The sulphonation mixture is then cooled and added to water and worked up for the sodium salt in the usual way. 13.5 parts of sodium salt were obtained, representing a yield of 23.5%.

Example III

A pyridinium sulphate solution in 75 parts oleum is prepared from 25 parts pyridine as described in Example I. 1.5 parts aluminum turnings are added to the solution and heated to

310°–320° C. After heating for one hour, 0.5 part aluminum and 16 parts oleum are added. This is repeated after the second and third hour of heating, and then the heating is continued for eight more hours. The sulphonation mixture is then cooled and added to water and worked up for the sodium salt in the usual way. 12.7 parts of sodium salt was obtained representing a yield of 21.6%.

Example IV

A pyridinium sulphate solution in 75 parts of oleum is prepared from 25 parts pyridine as described in Example I. Two parts of mercury sulphate are added to the solution and heated to 270° C. After an hour heating 16 parts of oleum and 1 part of mercury sulphate are added. The heating is continued, and the addition is repeated after an hour of heating. The heating is then continued and the reaction mixture is worked up as in Example I. The yield obtained is 68% of the theoretical.

It will be noted from the foregoing that our invention broadly comprises the periodical addition of oleum and a catalyst to a mixture of pyridinium, oleum and a catalyst, whereby increased yields are obtained over former processes, with decreased amounts of materials and at lower temperatures.

As already mentioned other metals than those described in the examples, may be used as catalyst in the sulphonation of pyridine without departing from the invention or sacrificing the advantages thereof. Therefore, we do not limit ourselves to the specifically mentioned times, temperatures, quantities, chemicals, or steps of procedure as these are given simply to describe our invention as set forth in our specification and claims, and they may be varied without going beyond the scope of our invention.

What we claim is:

1. In a process of sulphonating pyridine in the 3 position, the step which comprises the periodical additions of oleum and a member of the group of catalysts consisting of mercury, aluminum, magnesium and vanadium and their sulphates to a solution of pyridine sulphate in oleum under sulphonating temperatures and recovering the 3 pyridine sulphonic acid.

2. In a process of sulphonating pyridine in the 3 position, the step which comprises the periodical additions of oleum and mercury to a solution of pyridine sulphate in oleum at temperatures between 250°–320° C. and recovering the 3 pyridine sulphonic acid.

3. In a process of sulphonating pyridine in the 3 position, the step which comprises the periodical additions of oleum and magnesium to a solution of pyridine sulphate in oleum at temperatures between 250°–320° C. and recovering the 3 pyridine sulphonic acid.

4. In a process of sulphonating pyridine in the 3 position, the step which comprises the periodical addition of oleum and mercury sulphate to a solution of pyridine sulphate in oleum at temperatures between 250°–320° C. and recovering the 3 pyridine sulphonic acid.

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