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THE ELECTROLYTIC PREPARATION OF SEMICARBAZINE SULFATE

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In the course of a series of experiments planned for the quantitative study of the influence of various conditions on the cathodic reduction of organic compounds, it was found that the reduction of nitro-urea to semicarbazine in acid solution was not only suitable for this purpose but could also be made to give excellent yields of semicarbazine salts. Since nitro-urea can be made very easily from urea nitrate and since the present methods of preparing semicarbazine are rather unsatisfactory, it seems worth while to report an improved method that has been developed for preparing this useful reagent on a moderately large scale. Experiments described in this paper show that working with 50-75-g. lots of nitro-urea, it is possible to obtain consistent yields of semicarbazine sulfate amounting to 60–70%. The apparatus can be quickly assembled from readily available materials and the working time required is not excessive.

The electrolytic reduction of nitro-urea has been previously studied by Holroyd[1] who carried out the reduction on 10g. portions using iron electrodes and ammonium chloride solutions as the catholyte. The semicarbazine was isolated as benzalsemicarbazone and subsequently converted to the hydrochloride by the method of Thiele and Stange.[2] The yield did not exceed 60% and much time was required. Backer[3] carried out the reduction with tin-coated copper cathodes in a mixture of acetic and sulfuric acids and obtained a 74% yield on a small scale. Ochi[4] has more recently studied the reduction using lead cathodes and a 10% hydrochloric acid solution as the catholyte and recovering the semicarbazine hydrochloride by evaporation. The quantities used and the yield are not stated in the abstract.

Exploratory Experiments

As the previous work was not very systematic, it was first sought to find the best conditions for carrying out the reduction. A large number of runs were made on 20g. samples of purified nitro-urea suspended in 600 cc. of the catholyte in a reduction cell, smaller than, but essentially similar to the one described in the Experimental Part. The cathodes were cylindrical metal sheets of 450 sq. cm. area, except for mercury, which was a layer at the bottom of the cell and was 140 sq. cm. in area. The anodes

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[1] Holroyd, *J. Chem. Soc.*, **79**, 1326 (1901).

[2] Thiele and Stange, *Ann.* **283**, 21 (1894).

[3] Backer, *Rec. trav. chim.*, **31**, 1 (1912); *J. Chem. Soc.*, **102**, (i) 339 (1912).

[4] Ochi, Japan. pat. 39,219; *J. Chem. Soc.*, **122**, (i) 723 (1922).

of sheet lead were equal in area to the cathode and were immersed in 10–20% sulfuric acid as anolyte. In order to follow the reaction and determine its end the semicarbazine produced was estimated at frequent intervals by withdrawing 10 cc. of the catholyte, precipitating under standard conditions with benzaldehyde, and weighing the nearly insoluble benzalsemicarbazone. Parallel cathode potential measurements, taken with a Leeds and Northrup potentiometer against a 0.1 *N* mercurous sulfate electrode, were recorded in connection with the original purpose of the work and will be discussed at another time. With the above conditions constant, the following conditions were varied systematically, with the results noted.

Temperature.—Using a lead cathode, 10% hydrochloric acid as catholyte and operating at a current density of 0.03 amp. per sq. cm., the yields of semicarbazine after two hours were 16.0%, 34.4% and 35.7%, respectively, at temperatures of 24°, 10.5° and 4.0°. The most suitable temperature is, accordingly, 5–10°.

Nature of the Catholyte.—Operating at 5–10° the yields after 2.5 hours were 34.0%, 37.5%, 51.0%, 58.0% 66.3% and 69.2%, respectively, when using 10% acetic acid and 10% sulfuric acid, 10% hydrochloric acid, 5%, 10%, 15%, 20% sulfuric acid as catholytes. The best catholyte was, therefore, 15–20% sulfuric acid. Closely similar results were obtained when a mercury cathode was used in place of lead.

Nature of Cathode.—Operating as above, but with 15% sulfuric acid as catholyte, the yields after 2.5 hours were 48.0%, 52.8%, 66.4% and 69.6%, respectively, with cathodes of copper, nickel, lead and mercury. The yield with a mercury cathode (140 sq. cm. area) was not much greater than with one of lead (450 sq. cm. area) but as a cell using mercury is simpler, more nearly permanent and more easily cooled, it was adopted.

In supplementary experiments it was found that two additional factors were of importance in obtaining a good yield. First, the yield was increased by increasing the current density and reducing as rapidly as possible. Thus two comparable small-scale runs using 0.03 and 0.06 amps. per sq. cm., respectively, gave yields of 77% and 92%. The time required is also shortened by the greater current density. Second, it is necessary to keep the ratio of volume of catholyte in cubic centimeters to the area of the cathode in square centimeters as small as possible and preferably less than 3:1. Thus in comparative experiments in which 1500, 1200 and 600 cc. of catholyte were used with a mercury cathode 215 sq. cm. in area, the respective yields were 45%, 65% and 69%. This would indicate that the yield might be increased by further decreasing the volume-area ratio. This, however, is not practicable due to the difficulty of keeping the temperature within the required range when working with small volumes. For the same reason current densities much higher than 0.06 amps. per. sq. cm. are not suitable.

With the results of the experiments described above in mind a series of larger runs was carried out. The apparatus and results are described in the Experimental Part. The yield is somewhat smaller when working on a large scale due to the necessary changes in the dimensions of the cell. For reasons of convenience no attempt was made to design a special cell. The use of less pure grades of nitro-urea also decreased the yield slightly but materially shortened the time required.

Experimental Part

Apparatus.—The cell used in all the large scale experiments consisted of a sturdy glass jar, having a diameter of 16.5 cm. and 3 liters' capacity, in which was suspended, near the side, an 8 × 21 cm. porous cup such as is used in the Daniel cell. The anode, a narrow, coiled strip of lead equal in area to the cathode, was placed inside the cup. The cathode was a shallow layer of mercury in the glass vessel and had an area of 215 sq. cm. Connection with the cathode was made through a glass tube filled with mercury and having a stout piece of platinum wire sealed in the lower end. An ammeter and a rheostat were placed in series with the cell. The current was taken from a battery of storage cells. To operate one cell of the type described the battery must be capable of delivering at least 15 amps. at 8 volts. An efficient mechanical stirrer was arranged so that the catholyte was vigorously agitated. The cell was surrounded by an ice-salt mixture.

Materials.—The mercury and the sulfuric acid were of C.P. grade, not specially purified. The nitro-urea was prepared from urea nitrate and sulfuric acid by the method of Thiele and Lachman[6] and for some of the experiments was purified by one crystallization from warm water. The product, which may contain traces of sulfates, is thus obtained in yields of 120–140 g. from 200 g. of urea nitrate. When purification is omitted the yield is slightly larger.

Reduction and Isolation Procedure.—In all, 14 experiments using 50 g. or more of the nitro-urea were carried out. Only the procedure finally adopted which gave consistent results, together with a more rapid optional method, need be described.

In the first series of experiments 50 g. of once-crystallized nitro-urea was suspended in 600 cc. of 20% sulfuric acid in the cathode compartment of the cell described above. The anolyte was 20% sulfuric acid. Stirring was started and when the temperature reached 5° current was passed at the rate of 0.06 amp. per sq. cm. calculated on the basis of the mercury surface. The temperature was held below 9°. As the reduction proceeded the nitro-urea gradually dissolved. Solution was usually complete at the end of four hours and the current was stopped after an additional half-hour.

[6] Thiele and Lachman, *Ann.*, **288**, 281 (1895).

The solution was then poured or siphoned off, filtered from a trace of insoluble matter, and evaporated with a good water pump at a temperature not higher than 45° and preferably somewhat lower, near the end. Under these conditions there was no decomposition. When the volume had been reduced to about 150 cc. the liquid was allowed to cool slowly, finally in ice water, whereupon the semicarbazine sulfate separated in well-formed crystals. These were collected on a hardened filter, washed with a little absolute alcohol and dried. The yield from several operations under the above conditions varied from 55 to 57 g. (67–70%). A small quantity of salt still remained in the mother liquor. A part of this was recovered by further evaporation of the combined residues from several runs, thus slightly increasing the yield. Except for careful temperature control, little attention is required during the reduction and evaporation.

Rapid Optional Procedure.—The above experiments, as noted, were carried out with once-crystallized nitro-urea. It was sought to shorten the time required by reducing the crude nitro-urea as obtained by pouring the original nitration mixture onto ice, filtering and washing once with cold water. In one experiment half of the crude, moist nitro-urea obtained from 200 g. of urea nitrate (moist weight, 100 g.; dry weight, 76 g.) was made up to 600 cc. with 20% sulfuric acid and reduced as before. Six hours was necessary to complete the reduction. Upon evaporation there was isolated 66.2 g. of practically pure semicarbazine sulfate. From the second half, 62.3 g. was obtained. The yield is, therefore, 51.3%, based on crude nitro-urea. Later experiments in which the nitro-urea was washed several times and air-dried before reduction gave yields only slightly lower than when recrystallized nitro-urea was used and considerable loss of time and material was thus avoided.

Since much of the time required is consumed during reduction an experiment was carried out in which three smaller cells of the same type as described above were connected in series. The reduction proceeded normally, giving yields in the three cells of 59%, 58% and 57%, respectively. When larger quantities of semicarbazine are required and if sufficient electrical energy is available, this procedure would seem desirable.

Summary

1. A simple procedure is described for the electrolytic reduction of nitro-urea to semicarbazine and the isolation of the latter as its sulfate in practical quantities.
2. The best results were obtained by reducing 50g. portions of nitro-urea in 20% sulfuric acid upon a mercury cathode, using a current density of 0.06 ampere per sq. cm. and a temperature of 5° to 9°; yield, 60 to 70%.
3. A more rapid optional method is also described.

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