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A CONVENIENT METHOD FOR THE PREPARATION OF GUANIDINIUM SULFATE FROM SULFUR TRIOXIDE—AMMONIA REACTION MIXTURE AND UREA

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A convenient method of preparing guanidinium sulfate in a good yield has been established, which makes use of the reaction between urea and SO_3-NH_3 reaction mixture under an atmosphere of ammonia, and a series of novel treatments of the reaction mixture thus obtained.

It is well-known that guanidinium ion is formed by the reaction of urea with aquo ammono sulfuric acids or their ammonium salts (amidosulfuric acid, ammonium amidosulfate, ammonium imidodisulfate,etc.) or sulfur dioxide in the presence or the absence of ammonia.1),2),3),4) The auther has reported a convenient method of synthesizing guanidinium ion in a high yield (above 70%, based on urea) from urea by its reaction with SO_3-NH_3 reaction mixture in the presence of ammonia at 1 atm.5) However, no report has been published concerning practical methods of separating a useful guanidinium salt from these reaction mixtures which contain guanidinium ion in the form of more than two salts, such as amidosulfate, imidodisulfate, and sulfate. The present communication is concerned with a simple and convenient method of preparing guanidinium sulfate from such reaction mixtures without loss of guanidinium ion.

This investigation was undertaken on the basis of the following considerations : (a) each reaction mixture essentially consists of guanidinium, ammonium, sulfate, amidosulfate, and imidodisulfate ions. (b) the last two ions in the reaction mixture can be easily hydrolyzed in the presence of sulfuric acid (produced by the hydrolysis of imidodisulfate ion or added) at temperature above 100 °C in a closed vessel to afford a mixture consisting of the remaining and hydrogen ions. (c) when the hydrolyzed reaction mixture, dissolved in water, is treated with calcium hydroxide, a solution containing guanidinium sulfate and ammonium hydroxide will be obtained, and calcium sulfate dihydrate and excess calcium hydroxide can be filtered off. (d) when the solution thus obtained is treated with carbon dioxide, ammonium hydroxide and remaining calcium hydroxide are converted into their carbonates. (e) after removal of calcium carbonate by filtration, ammonium carbonate can be removed by heating the solution to leave guanidinium sulfate without decomposition of guanidinium ion.

A typical procedure is as follows. A reaction mixture between ammonia and sulfur trioxide [composition: ammonium ion, 16.5; imidodisulfate ion, 58.7; amidosulfate ion, 12.8; sulfate ion, 5.3; acidic material (as SO_3), 5.4%] , 85.6g, was allowed to react with 22.2g of urea at 260 °C for 12 min in the presence of ammonia according to the method previously reported.5) Five grams of the resulting mixture [108.47g; composition: guanidinium ion (70.6% yield, based on urea): 14.4, ammonium ion: 14.5, imidodisulfate ion: 23.5, amidosulfate ion: 13.9, sulfate ion: 30.6, cyanuric acid: 0.04, hot water-insoluble material: 1.8 %] and 1.5g of water, placed in a Teflon-lined pressure vessel (inner volume: ca. 25 ml), were heated in an air bath at 150 °C for 120 min. The mixture⁶⁾ thus obtained was then transfered to a beaker with water and treated with 3.501g of calcium hydroxide with stirring at room temperature for 15 min. The mixture was then filtered, and the filtrate was adjusted to pH 8 by bubbling carbon dioxide. After filtering off calcium carbonate, the filtrate was heated almost to boiling until the evolution of ammonia had ceased. A small amount of guanidinium carbonate in the concentrated solution thus obtained was neutralized with dilute sulfuric acid, and the resulting solution was evaporated to dryness to give 1.338g of white crystals. The IR spectrum of this product was identical with that of authentic sample of guanidinium sulfate. The purity of the guanidinium sulfate thus obtained was 95.3%, and cyanuric acid was the principal impurity (Table 1). The yield (69.2%, based on urea) indicates that there was little loss of guanidinium ion during the series of treatments.

Table 1. Analysis of a final product

Guanidinium sulfate	95.3 %
Ammonium ion	0.02 %
Calcium ion	0.05 %
Excess sulfate ion	0.02 %
Amidosulfate ion	0.07 %
Imidodisulfate ion	0 %
Cyanuric acid	3.9 %

In conclusion, it is noted that guanidinium sulfate can be conveniently prepared in a relatively good yield from the cheap materials such as SO_3-NH_3 reaction mixture and urea. Details will be published in a separate paper.

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References

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6) When this mixture was neutralized with ammonia, filtered, and evaporated to dryness, the resulting white crystals (5.476g) contained guanidinium sulfate (23.9%), ammonium sulfate (73.8%), and cyanuric acid (0.99%). This analysis indicates that the cyanuric acid content increased after the hydrolysis. This increase is probably due to the change of the ammelide contained in the hot water-insoluble part into cyanuric acid by hydrolysis in the presence of hydrogen ion.

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