PREPARATION OF GUANIDINE NITRATE.[1]

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When the paper of Werner and Bell[2] appeared in which the preparation of guanidine thiocyanate is described by the heating together of dicyandiamide and ammonium thiocyanate, it occurred to us that guanidine nitrate might perhaps be prepared similarly by the heating together of dicyandiamide and ammonium nitrate. Experiment quickly confirmed the belief, and the yields were found to be excellent.

Guanidine thiocyanate is deliquescent, difficult to purify, and unpleasant to handle. The nitrate is not deliquescent; it is easy to purify, and offers advantages to the worker who wishes an easily made salt of guanidine. For the explosive industry the nitrate possesses another great advantage, for nitroguanidine prepared from the thiocyanate still contains traces of sulfur compounds and is not fit for use in nitrocellulose powder since it impairs the powder's stability and causes it to blister on storage. Nitroguanidine may be prepared in excellent yield simply by dissolving guanidine nitrate in conc. sulfuric acid and pouring the solution into water. Studies on the preparation of the nitroguanidine by this method and of its reaction with and solubility in sulfuric acid of various concentrations are now practically completed at this laboratory and will form the subject of a later communication.

In a preliminary experiment dicyandiamide and two molecular equivalents of ammonium nitrate were heated together in a test-tube in an oil-bath at 160° until the mass which first fused had become practically solid again at that temperature. The product was found to consist almost entirely of guanidine nitrate. When this result was discussed in March 1921 with the chemists of the Fixed Nitrogen Research Laboratory, it appeared that the paper of Werner and Bell had induced Mr. Blair of that laboratory to try a similar experiment. He had worked at a lower temperature (135°) and had obtained no guanidine but had obtained the nitrate of biguanide. A reaction similar to this had long ago been noted by Smolka and Friedreich[3] who obtained biguanide chloride by heating together dicyandiamide and ammonium chloride in alcoholic solution in a sealed
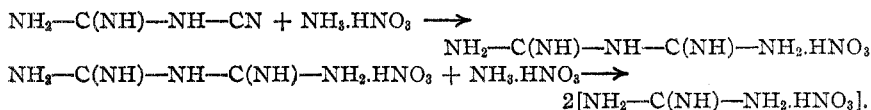
[2] Werner and Bell, *J. Chem. Soc.*, **118**, 1133 (1920).
[3] Smolka and Friedreich, *Monatsh.*, **9**, 228 (1888).

tube. They found also,[4] as did Bamberger and Dieckmann later,[5] that the same materials yielded biguanide chloride if simply melted together. Rathke,[6] even earlier, had actually obtained guanidine by the reaction; from the heating of dicyandiamide and ammonium chloride in aqueous solution at 150° he obtained ammelide and the chlorides of biguanide and of guanidine. Blair suggested that perhaps one molecule of ammonia added to dicyandiamide to form biguanide and that the biguanide reacted with a second molecule of ammonia to form guanidine. We have verified these suggestions by experiment. Since chance had led us first to prepare guanidine nitrate, the chemists of the Fixed Nitrogen Research Laboratory very kindly agreed, in order to avoid duplication of effort, to experiment no more on the formation of guanidine nitrate by the heating together of ammonium nitrate[7] and dicyandiamide but to devote their attentions to other methods for the preparation of guanidine nitrate from lime-nitrogen for the study of which the peculiar facilities of their laboratory were especially adapted.

The mechanism of the reaction is as follows.

$$NH_2\text{---}C(NH)\text{---}NH\text{---}CN + NH_3.HNO_3 \longrightarrow$$
$$NH_2\text{---}C(NH)\text{---}NH\text{---}C(NH)\text{---}NH_2.HNO_3$$
$$NH_2\text{---}C(NH)\text{---}NH\text{---}C(NH)\text{---}NH_2.HNO_3 + NH_3.HNO_3 \longrightarrow$$
$$2[NH_2\text{---}C(NH)\text{---}NH_2.HNO_3].$$

We have demonstrated the truth of these equations by showing (1) that dicyandiamide and two molecules of ammonium nitrate at 120° yield biguanide nitrate, (2) that the same materials at 160° give guanidine nitrate, and (3) that biguanide nitrate and ammonium nitrate in molecular proportions fused together give guanidine nitrate. The reaction therefore is not dependent upon the depolymerization of dicyandiamide as Werner and Bell have supposed.

Since the biguanide nitrate which is first formed by the addition of one molecule of ammonium nitrate to one of dicyandiamide is strongly basic and tends to react with a second molecule of ammonium nitrate to form the normal nitrate and to liberate ammonia, we found it expedient in preparing guanidine nitrate to work with a slight excess, i. e., with 2.2 mols. of ammonium nitrate.

When a small quantity of a mixture of dicyandiamide and ammonium nitrate in molecular porportions is carefully melted in a test-tube, ammonia is given off and the product if cooled promptly contains a large quantity

[4] Smolka and Friedreich, *Monatsh.*, **10**, 86 (1889).

[5] Bamberger and Dieckmann, *Ber.*, **25**, 545 (1892).

[6] Rathke, *ibid.*, **18**, 3107 (1885).

[7] German pat. 222,552 of October 30, 1908, ought to be noted in this connection. It describes the preparation of guanidine salts by the dry heating together of dicyandiamide and ammonium salts *in molecular proportions*. We find that two molecules of the ammonium salt are necessary for the reaction and that the product is two molecules of the guanidine salt.

of nitrate of biguanide. If, however, a larger quantity of the same mixture, say 150 g., is heated in a beaker carefully with a free flame, a violent reaction sets in at the moment that the mass fuses clear, much heat is disengaged, ammonia comes off abundantly, a white substance precipitates in the hot liquid and somewhat more than half of the dicyandiamide is converted into ammeline (along with a little ammelide) while somewhat less than half appears in the form of guanidine nitrate.

A mixture of one mol. of dicyandiamide and two mols. of ammonium nitrate heated at 120° sinters together after a time and assumes a porridge-like consistency. After 6 hours' heating the mass contains considerable unchanged dicyandiamide and ammonium nitrate together with biguanide nitrate and a small quantity of guanidine nitrate. At 130° the same mixture fuses within an hour to a clear colorless liquid which undergoes no apparent change during a further 2 hours of heating, and yields considerable guanidine and biguanide. At 120° in the autoclave with water the same mixture, after 2 hours' heating, yields the same products as when the heating is carried out for a longer time in the absence of water.

A mixture of dicyandiamide and 2.2 mols. of ammonium nitrate heated at 160° fuses to a colorless liquid which soon begins to deposit crystals and becomes practically solid at the end of 2 hours' heating. From the product we have isolated guanidine nitrate in amounts equal to more than 85% of the calculated yield. The same materials heated in an autoclave at 160° for 2 hours with water or with alcohol give practically the same yields of guanidine nitrate, but alcohol appears to be no better than water for the purpose. A temperature higher than 160° appears to offer no advantage.

Experiments with the nitrates of substituted ammonias are now under way in this laboratory.

Discussion of Experiments.

Sealed Tube Experiments.—Five g. of dicyandiamide, 9 g. of ammonium nitrate, and 11 cc. of absolute alcohol were heated together in a sealed tube for 1 hour at 160°. When the tube was opened, a slight odor of ammonia was perceptible and the contents gave off a disagreeable putrid odor similar to that which is produced in the synthesis of malonic ester from chloro-acetic acid. The contents of the tube consisted of white crystalline shiny plates. On recrystallization from moist alcohol these yielded 12 g. of guanidine nitrate, m. p., 212° (pure guanidine nitrate, m. p., 215–216°); calculated yield, 14.5 g.; actual yield, 82.7%. The product was identified as guanidine nitrate by its own melting point, by the melting point of its picrate, and by the fact that it yielded nitroguanidine on treatment with sulfuric acid.

A similar experiment in which 10 cc. of water was used instead of the alcohol yielded 13 g. of guanidine nitrate, m. p., 212°; or 89.6%. We conclude that water is preferable to alcohol.

Autoclave Experiments.—For the purpose of determining the best conditions for the reaction, other experiments were carried out in a small autoclave of about 100cc. capacity. After the autoclave had been closed, it was immersed in a bath of heated

oil the temperature of which was determined by means of a thermometer. After the heating, the autoclave was cooled promptly by immersion first in oil and later in cold water. 16.8 g. of dicyandiamide, 33.6 g. of ammonium nitrate, and 20 cc. of water were heated at 130° for 1 hour. The first crude product amounted to 45 g. and gave a test for biguanide nitrate. Recrystallized from alcohol it was found to consist in large part of guanidine nitrate and the first crystal fraction gave no test for biguanide. The mother liquors contained biguanide, and, worked up by recrystallization from alcohol and from water, yielded about 2 g. of biguanide nitrate.

A similar experiment at 160° for 2 hours yielded, after the product was recrystallized from water, 42 g. of guanidine nitrate, m. p., 206°, and 1.2 g. of white insoluble material (ammeline and ammelide). The calculated yield was 48.8 g. of guanidine nitrate, the actual yield, 86.0%. An experiment for a longer time, 3 hours at 160°, gave practically the same result, 42 g. of guanidine nitrate, m. p., 209°, and 1.1 g. of the white insoluble by-product.

A similar experiment at a higher temperature, 180° for 2 hours, gave the same yield of guanidine nitrate, 42 g., m. p. 208-209°, but it yielded considerably more, 4.8 g., of the insoluble white material.

Fusion Experiments.—An experiment without any solvent gave results as gratifying as those which were obtained from the autoclave. Five g. of dicyandiamide and 9 g. of ammonium nitrate were mixed in a dry test-tube and heated in the melting-point bath at 160° for 2 hours. The mass first fused to a colorless liquid and ammonia was evolved. It soon began to deposit crystals which increased in amount as the heating was continued, and the material became an almost solid mass at the end of an hour. The heating was continued for another hour in order to drive the reaction to completion. The product was entirely soluble in water and yielded, on recrystallization from this solvent, 13 g. of guanidine nitrate, m. p. 210°; or 89.6%.

An experiment at a lower temperature yielded considerable biguanide. A mixture of 4.2 g. of dicyandiamide and 10 g. of ammonium nitrate was heated at 130° in a dry test-tube in the oil-bath. At the end of half-an-hour the mass had melted (except for a few crystals) to a colorless liquid. No further change appeared when the heating was continued for an hour. The product was readily soluble in water. Half of the resulting solution, treated with ammonium picrate, yielded 2.0 g. of guanidine picrate, m. p. 310-315°. The other half, treated with ammoniacal copper nitrate, yielded 0.6 g. of the characteristic copper-biguanide nitrate. When ammoniacal copper nitrate was added, a flocculent precipitate was produced but its color could not be seen because of the intense blue color of the solution. The precipitate was filtered off on asbestos and rinsed with water. The contents of the filter, asbestos and all, boiled up with water and filtered through paper, yielded a bright purple solution which deposited on cooling rose-colored needles of copper-biguanide nitrate.

A mixture of 84 g. of dicyandiamide and 80 g. of ammonium nitrate was carefully warmed in a Pyrex beaker. The mass started to melt readily enough, but at the moment when it fused clear, even though the flame was withdrawn, a violent reaction set in, ammonia fumes were given off in great abundance, the mass heated up greatly, effervesced, and deposited a white solid. After cooling, the product resembled chalk or porcelain. Worked up with water, it yielded 62 g. of guanidine nitrate, m. p. 209°, 56 g. of ammeline and 6.3 g. of amelide. The mother liquors gave no test for biguanide with ammoniacal copper nitrate.

Half a gram each of biguanide nitrate and ammonium nitrate were brought to fusion together in a dry test-tube. The product, taken up in water and precipitated with ammonium picrate, yielded guanidine picrate, m. p. 316-320° with decomposition.

Summary.

Guanidine nitrate may be obtained in excellent yield by heating dicyandiamide for 2 hours at 160° with slightly more than 2 molecules of ammonium nitrate, using either the dry materials alone or the materials and water in an autoclave.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

AN INDIRECT METHOD OF PREPARATION OF ORGANIC MERCURIC DERIVATIVES AND A METHOD OF LINKING CARBON TO CARBON.

Preliminary Report.[1]