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PROCESS FOR PREPARATION OF TRIAMINOGUANIDINE AND ITS SALTS

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This invention relates to a new method for the preparation of a guanidine derivative, particularly triaminoguanidine free-base and its nitrate, chlorate, picrate, perchlorate and halogen salts. These compounds offer special advantages when used as propellant ingredients in guns or rocket motors and may likewise be used as explosive materials or as intermediates for the preparation of explosives.

These advantages are derived from the fact that these compounds contain a high percentage of nitrogen in the form of a hydrazine linkage which is thermodynamically favorable from the standpoint of propulsion. Furthermore, the triaminoguanidine nitrate, chlorate, picrate and perchlorate salts have a good thermal stability and are compatible with other propellant or explosive ingredients. Triaminoguanidine can be isolated as its free-base and it has been found to react readily with metals such as aluminum, magnesium, beryllium and boron to give high energy rocket fuels.

Heretofore, various methods have been suggested for the preparation of triaminoguanidine derivatives but most of them require the formulation of guanidine or guanidine derivatives such as aminoguanide which is subsequently reacted with hydrazine. In other instances triaminoguanidine has been obtained by reacting cyanogen chloride and hydrazine under closed conditions. These methods have been found to be uneconomical and rather unadaptable to large scale production.

It is an object of this invention to produce triaminoguanidine free base and triaminoguanidine salts by a novel method.

It is a further object of this invention to produce guanidine derivatives that are in themselves or when combined with other compounds adapted to be used as propellants, explosives and the like.

It has been found that disadvantages of the prior art may be overcome by making use of a readily available material such as calcium cyanamide as the starting material. This invention discloses a novel method for the preparation of triaminoguanidine nitrate by the aqueous fusion of calcium cyanamide and hydrazine nitrate in a temperature range of 90° to 130° C. for a period of one to four hours. Another aspect of this invention is to demonstrate that this method is also applicable to the preparation of triaminoguanidine hydrochloride by following a similar procedure except that hydrazine hydrochloride is substituted for the hydrazine nitrate.

A particular embodiment of this invention involves the reaction of an aqueous solution of calcium cyanamide with an excess of hydrazine nitrate. It has been found that a yield of 95% or better of triaminoguanidine nitrate can be realized. The parameters of time, temperature of the reaction and excess of hydrazine nitrate have been evaluated. Experiments have been performed using 25% to 225% excess of hydrazine nitrate combined with a reaction time from 30 minutes to four hours, while varying the reaction temperature between 90° and 130° C.

It has been found that as the excess of hydrazine nitrate is increased the time for the completion of the reaction is decreased. The best yield of triaminoguanidine nitrate was obtained with a 225% excess of hydrazine nitrate and a reaction time of 3.5 hours at 105° C. After completion of the reaction the calcium ion is removed by the addition of a carbonate ion and the unreacted hydrazine nitrate is almost entirely recoverable.

A further aspect of the present invention is to demonstrate the preparation of a new compound called triaminoguanidine free-base. This compound may be obtained in a crystalline form, by passing the triaminoguanidine nitrate or hydrochloride through an ion exchange resin followed by precipitation with dimethyl formamide. An even simpler method consists of neutralizing the triaminoguanidine nitrate or hydrochloride salt in an aqueous solution with sodium hydroxide, then upon the addition of dimethyl formamide, the white crystalline triaminoguanidine free-base is precipitated out. In contact with the mother solution, the white crystalline triaminoguanidine free-base was found to be very stable, while in contact with air the white crystalline material rapidly turns pink. Experiment indicates that one of the major decomposition products of triaminoguanidine free-base is diaminourea.

Experiments in this area further demonstrate that other salts of triaminoguanidine such as hydrobromide, picrate and perchlorate can be prepared by the addition of the appropriate acid to an aqueous solution of the free-base. It has been further demonstrated that the free-base under proper conditions reacts with such metals as aluminum, magnesium, beryllium and boron when in the presence of a solvent such as benzene, toluene, xylene, methyl formate or ethyl formate. Based upon their thermochemical properties these organo-metallic compounds are of potential interest as highly energetic rocket fuels. Furthermore, the thermochemical properties of the nitrate, picrate and perchlorate salts suggest that they may find application in an artillery propellant, gas generator propellants and other explosive compositions.

The following examples set forth some of the specific embodiments of this invention, but are not to be construed as limiting this invention.

EXAMPLE 1

A 90% solution prepared from 675 g. of hydrazine nitrate and 75 g. of water was heated to 80°–85° C. in a beaker. With constant stirring 149.5 g. of calcium cyanamide (53.5% purity) was added in small increments and the temperature raised and maintained at 105°–110° C. After stirring continuously for 3.5 hours, 1.5 liters of water were added followed by 240 g. of ammonium carbonate monohydrate. The mixture was heated to 85° C. and filtered while hot through a steam jacketed funnel. The precipitate was washed once with 100 ml. of hot water, and the combined filtrate and washing were chilled in an ice bath. The crystals of triaminoguanidine nitrate were filtered, washed with cold water, and dried under a vacuum over phosphorous pentoxide. The weight of the product was 159 g. which represented a 92.5% yield based on calcium cyanamide.

EXAMPLE 2

A 90% solution of hydrazine nitrate was prepared by the addition of 6.4 g. of water to 57.8 g. (225% excess) of hydrazine nitrate. The receptable containing the solution was placed in an oil bath maintained at 110° C. and 7.25 g. of calcium cyanamide (68.94% purity) was added in small portions. The reaction was continued with constant stirring for 2.5 hours after which 90 ml. of water was added and the mixture heated to 85° C. The calcium was precipitated by the careful addition of 15 g. ammonium carbonate monohydrate, to prevent excess frothing.

The mixture was filtered hot through a steam jacketed funnel and the precipitate washed with 10 ml. of hot water. The combined filtrate and washing were chilled in an ice bath. The crystals of triaminoguanidine nitrate formed, were filtered with suction, washed with cold water and dried in an oven at 100° C. for two hours. The weight of the product was 9.91 g. which represents a 94.8% yield based on calcium cyanamide.

EXAMPLE 3

A 90% solution of hydrazine nitrate was prepared by the addition of 6.4 g. of water to 57.9 g. (225% excess) of hydrazine nitrate. The solution, contained in a beaker, was placed in an oil bath maintained at 120° C. and 7.25 g. of calcium cyanamide (68.94% purity) and added portionwise. The reaction was continued with stirring for two hours after which 90 ml. of water and 15 g. of ammonium carbonate monohydrate were added. The mixture was filtered hot through a steam-jacketed funnel and the precipitate washed with 10 ml. of hot water. The combined filtrate and washing were chilled in an ice bath. The crystals of triaminoguanidine nitrate were filtered, washed with cold water, and dried in an oven at 100° C. for two hours. The weight of the product was 9.74 g. which represents a 93.2% yield based on calcium cyanamide.

EXAMPLE 4

A 90% solution of hydrazine nitrate was prepared by the addition of 6.4 g. of water to 57.8 g. (225% excess) of hydrazine nitrate. The beaker containing the solution was placed in an oil bath maintained at 130° C. and 7.25 g. of calcium cyanamide (68.94% purity) were added portionwise. The reaction continued with stirring for 1.5 hours after which 90 ml. of water were added. The mixture was heated to 85° C. and 15 g. of ammonium carbonate monohydrate were added and the mixture was filtered hot through a steam-jacketed funnel and the precipitate washed with 10 ml. of hot water. The combined filtrate and washing were chilled in an ice bath. The triaminoguanidine nitrate was filtered, washed with cold water and dried in the vacuum desiccator over phosphorous pentoxide. The weight of the product was 9.61 g. which represents 92.0% yield based on calcium cyanamide.

EXAMPLE 5

A 90% solution of hydrazine hydrochloride was prepared by the addition of 3.4 g. of water to 30.6 g. of hydrazine hydrochloride (200% excess). The beaker containing the solution was placed in an oil bath maintained at 110° C. and 5.94 g. of calcium cyanamide (67.4% purity) were added portionwise. The reaction was continued with constant stirring for 2.5 hours then 50 ml. of water was added. The mixture was heated to 85° C. and 11.4 g. of ammonium carbonate monohydrate were added. The precipitate was removed while hot by filtration through a steam jacketed funnel and washed with 10 ml. of hot water. The combined filtrate and washing were chilled in an ice bath. The crystals of triaminoguanidine hydrochloride were filtered, washed with a small portion of cold water and dried in the oven at 100° C. The weight of the product was 4.5 g. which represents a 64% yield based on calcium cyanamide.

EXAMPLE 6

Five grams of triaminoguanidine nitrate were dissolved in 20 ml. of water containing 1.2 g. of sodium hydroxide and 40 ml. of dimethyl formamide were added. While vigorously shaking the solution was quickly chilled in an acetone-Dry Ice bath and then placed in a refrigerator overnight. The crystals of triaminoguanidine formed were filtered, washed with cold ethanol and ethyl ether, and sucked dry. The weight was 2.0 g. representing a 66.5% yield.

EXAMPLE 7

Ten grams of triaminoguanidine were dissolved in 30 ml. of water containing 2.4 g. of sodium hydroxide and 60 ml. of dimethyl formamide were added. The solution was quickly chilled in an acetone-Dry Ice bath and placed in a refrigerator overnight. The crystals triaminoguanidine which deposited were filtered, washed with cold ethanol and ethyl ether, and sucked dry. The weight of the product was 4.6 g. representing a 74% yield.

EXAMPLE 8

Five grams of triaminoguanidine hydrochloride were dissolved in 20 ml. of water containing 1.45 g. of sodium hydroxide, and dimethyl formamide was added. The solution was chilled in an acetone-Dry Ice bath. After vigorous shaking a precipitate was formed, and the flask was placed in a refrigerator overnight. The crystals of triaminoguanidine which deposited were filtered, washed with ethanol and ethyl ether, and sucked dry. The weight of the product was 3.4 g. representing a 91.5% yield.

EXAMPLE 9

Thirty grams of triaminoguanidine nitrate, dissolved in water was passed through an ion-exchange column containing Amberlite IRA 401 in the hydroxy form. The aqueous effluent was flash-evaporated at room temperature to a low volume (about 130 ml.) and 260 ml. of dimethyl formamide were added. The solution was quickly chilled in an acetone Dry-Ice bath, and crystals of triaminoguanidine precipitated immediately upon vigorous shaking. The flask was placed in a refrigerator overnight. The crystals of triaminoguanidine were filtered, washed with cold ethanol and ethyl ether, and sucked dry.

EXAMPLE 10

An aqueous solution of triaminoguanidine nitrate was passed through an ion-exchange column containing Amberlite IRA 401 in the hydroxy form. The effluent was acidified with 72% perchloric acid and the solution was flash evaporated to dryness. The crystals of triaminoguanidine perchlorate were dissolved in a small amount of water and reprecipitated by the addition of isopropanol. M.P. 134°–135° C. Chloride analysis: calculated 17.35%; found 17.70%.

EXAMPLE 11

A portion of the effluent containing an aqueous solution of triaminoguanidine prepared by ion-exchange technique was added to a saturated aqueous solution of picric acid. The solution was heated to boiling then cooled to room temperature. The crystals of triaminoguanidine picrate were filtered, washed with water and then recrystallized from water. M. P. 170.5°–171.5° C. Nitrogen analysis: calculated 37.84%; found 37.61%.

EXAMPLE 12

A saturated aqueous solution of picric acid was added to a solution triaminoguanidine nitrate in water. The mixture was heated to boiling and then cooled to room temperature. The crystals of triaminoguanidine picrate were filtered, washed with cold water and dried under vacuum over phosphorous pentoxide. M.P. 170° 171° C. Nitrogen analysis: calculated 37.84%; found 36.48%.

EXAMPLE 13

A 90% solution of hydrazine hydrochloride was prepared by the addition of 7.5 g. of water to 67.59 g. of hydrazine hydrochloride (225% excess). The beaker containing the solution was placed in an oil bath maintained at 110°–115° C. and 14.2 g. of commercial grade calcium cyanamide (56.28% purity) were added. The mixture was heated to about 85° C. and 228 g. of ammonium carbonate monohydrate were added. The mixture was filtered while hot through a steam-jacketed funnel, and the precipitate washed with 10 ml. of hot water. The combined washing

and filtrate were chilled in an ice bath. The crystals of triaminoguanidine hydrochloride were filtered, washed with a small portion of cold water and dried in the oven at 100° C. The weight of the product was 10.5 g. representing a 75% yield.

EXAMPLE 14

A 90% solution of hydrazine nitrate was prepared by the addition of 19.2 g. of water to 172.8 g. (225% excess) of hydrazine nitrate. The beaker containing the solution was placed in an oil bath maintained at 110° C. and 26.7 g. of calcium cyanamide (56.28% pure) were added portionwise. The reaction was continued with constant stirring and after 2.5 hours, 250 ml. of water and 17.0 g. of Dry Ice were added. The mixture was heated to 85° C., filtered while hot through a steam-jacketed funnel and the filtrate chilled in an ice bath. The crystals of triaminoguanidine nitrate were removed by filtration, washed with cold water and dried in an oven at 100° C. The weight of the product was 29.5 g. representing a 94.2% yield based on calcium cyanamide. Analysis of the mother liquor showed that about 10% of the excess hydrazine nitrate had been lost during the reaction. Consequently, to compensate for this loss, and for the hydrazine nitrate which had been used in the reaction 77.2 g. were added to the mother liquor, then 26.7 g. of calcium cyanamide (56.28% pure) were added and the reaction repeated as previously described. The yield of triaminoguanidine nitrate was 94.6% of theoretical, and upon evaporation of the mother liquor 90% of the hydrazine nitrate was recovered.

These examples indicate the range of the process developed herein and the products made possible by this invention.

What is claimed is:

1. A process for the preparation of triaminoguanidine derivatives comprising treating a hydrazine compounded with a material selected from the group consisting of a triaminoguanidine nitrate, a hydrochloride, a perchlorate, a picrate, a halide in an aqueous solution with calcium cyanamide, precipitating the calcium by the addition of ammonium carbonate monohydrate, and removing the calcium precipitate by filtration to obtain the triaminoguanidine derivative.

2. A method for the preparation of triaminoguanidine salts comprising fusing an excess of hydrazine compounded with a material selected from the group consisting of a triaminoguanidine nitrate, a hydrogen chloride, a perchlorate, a picrate, and a halide in an aqueous solution with calcium cyanamide in a temperature range of 90° to 130° C. for a period of one to four hours, precipitating the calcium by the addition of ammonium carbonate monohydrate, and removing the calcium precipitate by fitration to obtain the selected salt of triaminoguanidine.

3. A process for the preparation of triaminoguanidine derivatives comprising heating a hydrazine compounded with a material selected from the group consisting of a triaminoguanidine nitrate, a hydrochloride, a perchlorate, a picrate, and a halide in an aqueous solution to 80°–85° C., adding calcium cyanamide in small increments and maintaining the temperature at 105°–110° C., stirring the mixture continuously for 3.5 hours, diluting the mixture with water followed by the addition of ammonium carbonate monohydrate to precipitate the calcium, chilling the filtrate in an ice bath to produce crystals of triaminoguanidine of selected compound and separating the crystals from the solution.

4. A process for the preparation of triaminoguanidine nitrate comprising heating hydrazine nitrate in an aqueous solution to 80°–85° C., adding calcium cyanamide in small increments while maintaining the temperature at 105°–110° C., stirring the mixture continuously for 3.5 hours, diluting the mixture with water followed by the addition of ammonium carbonate monohydrate to precipitate the calcium, heating the mixture to 85° C. and filtering while hot, chilling the filtrate in an ice bath to produce crystals of triaminoguanidine nitrate, and separating the crystals from the solution.

5. A process for the preparation of triaminoguanidine derivatives comprising heating a 90% solution, containing an excess of hydrazine compounded with a material selected from the group consisting of a triaminoguanidine nitrate, a hydrochloride, a perchorate, a picrate, and a halide, to 110° C. and maintaining that temperature, adding calcium cyanamide in small increments and continuing the reaction for two to three hours with constant stirring, diluting the solution with water, adding Dry Ice and heating to 85° C., filtering the solution while hot, chilling the filtrate in an ice bath to precipitate the crystals of the selected derivative of triaminoguanidine, removing the crystals by filtration, adding to the filtrate a sufficient amount of the selected hydrazine compound to compensate for the amount lost in the reaction and to maintain an excess thereof, treating again with calcium cyanamide to produce an equally high yield of crystals of the selected derivative of triaminoguanidine and recovering by evaporation of the filtrate a 90% yield of the selected hydrazine compound.

6. A process for preparing guanidine derviatives comprising treating a material selected from the group consisting of triaminoguanidine nitrate, hydrochloride, perchlorate, picrate, and halide in an aqueous solution with an alkaline neutralizing agent, adding dimethyl formamide to precipitate the triaminoguanidine derivative crystals, and separating the crystals from the solution.

7. A process of preparing triaminoguanidine free base comprising treating a hydrazine compounded with a material selected from a group consisting of a triaminoguanidine nitrate, a hydrogen chloride, a perchlorate, a picrate, and a halide in an aqueous solution with calcium cyanamide, precipitating the calcium by the addition of ammonium carbonate, monohydrate, neutralizing the filtrate with sodium hydroxide, adding dimethyl formamide to precipitate triaminoguanidine free base crystals, and separating the crystals from the solution.

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