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nitroguanidine

Nitroguanidine

Nitramine of Guanidine

Nitroguanidine is relatively stable below its melting point but decomposes immediately on melting to form ammonia, water vapor and solid products. The gases from the decomposition of nitroguanidine are far less erosive than gases from other similar explosives.

Nitroguanidine is soluble in hot water and alkalis, and insoluble in ethers and cold water. NitroGuanidine has a detonation velocity of 7.65km/sec and is very insensitive, much more so than RDX, despite both being nitramines. This is because the amine donate an electron to the nitramine. A more accurate structure may be (-)O2N(+)N(-)C(NH2)=NH2(+), thus the stability is comparable more toward a highly stable nitrate anion than a typical nitramine.

Synthesis:

200g sulphamic acid and 124g urea were mixed in a shallow Pyrex bowl and placed into a fan forced kitchen oven. The mixture was left in the oven at 220°C for 2 hours, where it gave off some ammonia and melted into a clear liquid gradually thickening and forming a white semi-solid due to ammonium and guanidine sulphate separated of from the melt. This was then cooled and broken up to leave 302g of crude residue.

The crude residue was then blended with 240g of potassium hydroxide in 1L of methylated spirits for 30 minutes. This freed the guanidine and ammonia bases and precipitated potassium sulphate, 750ml of this free based alcohol solution was recovered by filtering the blended mixture.

The alcoholic solution of guanidine and ammonia was then neutralised with 70% nitric acid, this precipitated residual potassium hydroxide as its nitrate which was filtered out. On boiling down the alcohol to a concentrated solution, then evaporating dry, 84g of crude ammonium and guanidine nitrates was obtained.

50g of the crude mixture of nitrates was directly converted to nitroguanidine by slowly dissolving small portions into 75ml of 98% sulphuric acid, the temperature was maintained from -5 to +10°C throughout the addition which took approximately 1.5 hours. The milky solution (picture below) was left for 10 minutes at 10°C after the last addition, then poured into 500ml of iced water. On standing the nitroguanidine precipitated as small crystals (below) which were filtered and dried. Yield was 18.5g. A more powerful version involves nitrating "di"-guanidine, to obtain dinitro-diGuanidine. This has comparable stability to DADNE, and is almost as powerful.

Credit the user "Axt" for the pictures

DinitroBiguanide

DinitroGuanidine

Biguanide (diGuanidine) can be made by first fusing urea with with pyrosulfate, making guanylurea sulfate. This is then netralized with a strong base to leave free guanyl urea. The guanyl urea is then fused with sulfamic acid to obtain diguanidine sulfate, which can then be directly used in the nitration.

DinitroGuanidine

DinitroGuanidine

Dinitroguanidine is the product of nitration of nitroguanidine. The reaction rate is much faster with a 2% solution of N2O5 in HNO3. Dinitroguanidine dissolved in water solution, slowly hydrolyzes after prolonged standing to precipitate nitroguanidine. It is moderately soluble in both water and organic solvents and the solubility quickly increases on warming. At 20C its solubility in water is 53g/L, in ethyl acetate 86g/L. Its

Dinitroguanidine can be recrystallized form alcohol or acetic acid, being a sufficiently stable compound with a melting point of 169C. Nitroguanidine forms salts with alkali dissolved in alcohol. Under sufficient acidic conditions, Dinitroguanidine hydrolyzes to nitroguanidine, while under only moderately acidic conditions nitrourea is formed.

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Synthesis and some Properties of 1,2-Dinitroguanidine
A.A.Astrat'yev, D.V. Dashko
State Technological Institute,
St. Petersburg, Russia

DinitroGuanidine

Nitroguanidine was once used as a propellent in model rocket motors. The exhaust gases were cooler than other typical compositions, which made for safer operation.

Nitroguanidine can condense with an equal molar ratio of hydrazine hydrate

Nitroguanidine reacts with one equivalent of hydrazine hydrate to form nitroaminoguanidine, with a structure NH2NHC(=NH)NHNO2. This reacts with HCl and NaNO2 to make Nitro guanylazide in 75% yield, reduction of nitraminoguanidine with Zn dust makes **diaminoguanidine**.

Ammonium dinitroguanidine (the dinitroguanidine salt of ammonia) decomposes at 197 °C, and has an impact sensitivity greater than 10 Joules, and friction sensitivity greater than 252 Newtons. The calculated detonation velocity of this salt is 9066 m/sec, with calculated detonation pressure of 332 kbar, The detonation velocity was experimentally measured and is consistent with the calculated value. From these values, ammonium dinitroguanidine shows greater explosive performance than HMX.

3-amino-1-nitroguanidine nitrate (nitroaminoguanidine) has a detonation pressure of 419kbar and detonation velocity of 9750m/s at a density of 1.905 g/cm3.

Nitrate Salt of Nitroguanidine

When nitroguanidine is dissolved in hot, concentrated nitric acid and allowed to crystallize, the nitrate salt is deposited in thick rhombic shaped prisms m.p. 147°C , with decomposition. They lose nitric acid slowly in the air and yield α-Nitroguanidine when recrystallized from water.

A salt of nitroguanidine with dinitrourea is probably posible, having an elemental composition with the ratio CN4H4O3, and likely possessing a high density, but the dinitrourea in this adduct would likely degrade in the presence of water, since nitroguanidine is only a very weak base.

Dinitroguanidine is not any more thermally stable or resistant to impact than dinitrourea.

Guanidine from Urea

By heating urea, ammonium chloride, and aluminum sulfate together with ammonia under pressure, guanidine can be obtained. The reaction products are boiled with an ammonium hydroxide solution to precipitate out the aluminum hydroxide. The remaining clear filtrate contains guanidine hydrochloride, ammonium sulfate, unreacted urea, and unreacted ammonium chloride. Using equimolar amounts of NH4Cl and urea, with one third of a mole aluminum sulfate for every mole of urea, heated to 275degC, and subjected to 6.8 atmospheres of pressure, the yield of guanidine (relative to initial urea) was 28% after 30 minutes, and 34% after two hours. Using excess NH4Cl increased the yields further.

One possible route to prepare aminoguanidine may be to react hydrazine with melamine powder, which is widely available and easily obtainable. This would probably cause the melamine to hydrolyze.

Refluxing formic acid with aminoguanidine would likely form 3-amino-1,2,4-triazole, that could then easily be nitrated (using only 70%conc hot nitric acid) to form 3-amino,5-nitro-1,2,4-triazole (ANTA).

Diazotizing Aminoguanidine

If aminoguanidine is treated with a mineral acid and sodium nitrite, the product is guanyl azide.

$$\text{NH}_2\text{C(=NH)NHNH}_2 + \text{HNO}_2 \rightarrow \text{NH}_2\text{C(=NH)N}_3 + (2)\text{H}_2\text{O}$$

If diazotization is carried out in the presence of acetic acid and sodium acetate, then diazoaminotetrazolic acid results. (HN4C)NHN=N(CN4H) , where the compound contains two tetrazole rings)

In neutral aqueous solutions, tetrazolyl guanyltetrazene hydrate is formed. (Note that earlier sources falsely claim this compound is "guanylnitrosoaminoguanyl tetrazene")

$$(2) \text{NH}_2\text{C(=NH)NHNH}_2 + \text{HNO}_3 + (2)\text{HNO}_2 \rightarrow (\text{HN}_4\text{C})\text{N}=\text{NN}(\text{NH}_2)\text{NC(=NH)NH}_2 + (2)\text{NaNO}_2$$

Kommentare