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nitrolic acids

(this section also includes information on methazonates, a related class of compounds)

Nitroethane has an aci- form tautomer, CH3CH=NO2H, which is susceptible to oxidative nitration by nitrogen dioxide in an ether solvent.

Ethyl **nitrolic acid** (C2N2O3H4) was prepared by the action of potassium hydroxide and sodium nitrite on nitroethane (Meyer & Constam, 1882). The crystals are lightly yellow in color. Crystallization from chloroform or ether gives needle like crystals. Melting point of 62deg (might be deg Faranheit). Ethyl Nitrolate salt of silver has been prepared by partial nitration of acetone using moderately concentrated "red fuming" nitric acid, then neutralization with silver carbonate. Ethyl nitrolic acid forms bright red salts with bases.

Ethyl nitrolic acid undergoes oxidative nitration with nitrogen dioxide to form 1,1,1-trinitro ethane. Ethyl nitrolic acid shares a tautomer with 1-nitro,1-nitroso ethane. The can be oxidized with hydrogen peroxide to 1,1-dinitro ethane. The oxidation of 2,2-dinitro propane has been used to synthesize 1,1-dinitro ethane. Note that sodium nitrolate can be made by reacting 1-nitro,1-nitroso ethane with sodium hydroxide, and similiary, acidifying a nitrolate salt will cause 1-nitro,1-nitroso ethane to separate out.

2-Nitro propane reacts with nitrous acid to form a **pseudonitrole** (2-nitroso,2-nitro-propane) which is colourless in crystalline form (dimer) but blue when melted or in solution (some equilibrium of the monomer).

These reactions are notable in that only moderately concentrated nitric acid is required, 60-70%, the nitrgogen dioxide can be made from a separate solution of such acid and bubbled into the first, making "red fuming" nitric acid.

Alternatively, beginning with glyoxime O=CHCH=O, the di-nitrolate of this was made, first by condensation with NH2OH, then reaction with NO2 and KNO2. The formed K2C2(NO2)4, which is the same thing as the potassium salt of 1,1,2,2-tetranitro ethane (if this is acidified it leaves free tetranitroethane which is oil-soluble). This salt was treated with concentrated H2SO4 and HNO3 dissolved in CH2Cl2, which produced **hexanitro ethane** C2(NO2)6 in 92% yield.

Methylnitrolic acid [AgCHN2O2] silver salt is obtained from double displacement of the potassium nitrolate salt in 75% concentrated ethanol with AgNO3. The red-brown product is soluble in dilute NH4OH solution and gives a violet color. When warmed with acids, especially dilute HNO3 it forms silver fulminate.

It may be interesting to investigate a potential double salt of potassium chlorate and potassium nitrolate (cocrystallized together), mixing the fuel and oxidizer on an ionic level to give a much higher detonation velocity than a simple mechanical mix of chlorate with a fuel.

related reactions

"US patent 5043488: slow addition of nitric acid to acetone produces an unknown explosive". probably ethylnitrolic acid (1-Nitro-1-oximinoethane). CH3C(NOH)NO2

"was prepared by mixing acetone with nitric acid (of 24% concentration) and a little fuming HNO3 and allowing the mixture to stand for 8 days at room temperature. An ether extraction gave on evaporation some acetylmethylnitrolic acid

Beil 3,621 and R. Behrend & H. Tryller, Ann283,221- 3(1894)

"... right after the strong oxidation left behind was a clear, thick yellow oil of a pungent odor. According to Jahresbericht über Fortschritte der Chemie (1902), Behrend and Tryller, p. 1075-77 this oil contained one-third to half acetylmethylnitrolic acid (CH3.CO.C(NOH).NO2) (cryst., mp. 62 deg., very decomposable) and other byproducts, including pyruvic and oxalic acids. They say in the same instance methyethyl ketone affords acetic acid, formic acid, and considerable amounts of ethylnitrolic acid and 1,1-dinitroethane"

methazonate salts

Mercury methazonate, which is a compound similar to mercury fulminate, is formed from the reaction of the sodium salt of nitromethane with mercuric chloride.

Nitromethane quickly reacts with a concentrated solution of sodium hydroxide to form the sodium salt of methazonic acid (alternatively named sodium 2-nitroethanaloximate),

(2) CH3NO2 + NaOH HON=CHCH=NO2Na + (2) H2O

The dry sodium methazonate salt is highly shock-sensitive and can explode violently.

When nitromethane is mixed with a concentrated solution of ammonium hydroxide, after several hours the liquid develops a dark brown color and a crystal substance begins to form. The small crystals formed a colored and difficult to purify. In a bottle, 20 cc (cm3) of pure nitromethane is mixed with 8 cc of the ammonia solution, and ammonia gas is then bubbled into the mixture until it is completely saturated (until no more gas can dissolve). A cap is then placed on the bottle and the bottle is kept under 10degC for about a day. The crystals which separate out are then removed and gently crushed into a moist powder. The powder is placed on an unglazed clay tile to draw out the water and allowed to air dry. The residual liquid still in the bottle is again saturated with ammonia gas and the process is repeated as before. This mehod will yield about 12 grams of the crystal substance. The crystals are soluble in methanol, less soluble in ethanol, and nearly insoluble in ether or chloroform. When the crystals are heated, they decompose, producing some poisonous hydrogen cyanide gas.

The crystals are ammonium 2-nitroethanaloximate, with the formula NH4(+) C2H3N2O3(-). The structure can be written HON=CHCH=NO2(-).

The crystals can be redissolved in water and will react with a solution of silver nitrate to form a pale yellow precipitate. The precipitate is filtered and washed with a mixture of alcohol and water, then air dried. Heating the silver salt near 100degC causes it to explode. The salt easily dissolves in dilute solutions of nitric acid or ammonia. It has the formula AgC2H3N2O3.

If the 2-nitroethanaloximate ion is acidified, methazonic acid is formed with the structure: HON=CHCH2NO2. This is done by dissolving the ammonium salt in a solution with the corresponding ammount of dilute sulfuric acid (just enough to react), then extracting the acid with ether. The ether calutions is dried with CaCl2 and evaporated in a vacuum. Methazonic acid crystallizes into crystal plates, and readily changes into a red resinous substance. The acid is soluble in water, alcohol, ether,acetone, warm benzene, and chloroform. Solutions of the acid are colorless, but on standing after a short time, a dark red color develops, and then eventually changes into a red colored resin. The acids melts between 60-70 degC. During the heating there is partial decomposition, and as the heating is continued the clear crystals first turn red, then gradually darken. At 100degC gas is evolved. At 110degC the acid explodes, leaving a black residue.

Structure

Possible resonance structure for 2-nitroethanaloximate ion.

(-)O2N=CHCH=NOH <--> O2NC(-)CH=NOH <--> O2NC=CHN(-)OH

Nitroformate (O2N)2C=NO2(-), for example, is an aromatic ion (which is bright yellow colored as a result). During the formation of 2-nitroethanaloximate (from a base and nitromethane), a dark reddish-brown color slowly develops, although supposedly the pure crystals of 2-nitroethanaloximate salts are colorless. This would suggest that something in the solution has an aromatic structure, but it could just be entirely attributable to a polymerized byproduct.

There also exists the double (-2) charged 2-nitroethanaloximate. "Disodium methazonate was prepared by the action of concentrated sodium hydroxide on nitromethane and the free acid and the monosodium salt isolated..." Both the monosodium and disodium salts of 2-nitroethanaloxime, in addition to the free acid, have been prepared and isolated. Seems to be only a matter of pH. It stated that the lead salts are insoluble, which may suggest a (-2) charge, but there was no formula provided for this. There may be possible interpolyatomic ion aromaticity across hydrogen bonds, but it is not known whether this is the case, or if there is any aromaticity within a single polyatomic ion. It is also possible that interesting resonance states do not exist at all, in which case the molecule may have either of the structures below, O2NCH2CH=NO(-) , (-)O2N=CHCH=NOH

The structure of methazonates are related to **nitrolates**, the two compounds being isomers.

The first image below shows a possible dimer of two methazonate anions, with intermolecular aromaticity across and through hydrogen bonds. Perhaps this aromatic dimer has some equilibrium in solution, but is not favored by crystal packing in the solid crystalline form. This might explain why the alkaline nitromethane solutions turn dark red-brown (because of conjugated bonding), yet pure methazonate salts tend to be colorless. For psuedonitrosite compounds, nitroso groups on two different molecules are already known to dimerize, resulting in a color change.

The second image below shows possible resonance structures for the methazonate anion. This may explain why the oxime does not trimerize, and why the methazonate does not condense further with another molecule of nitromethane.

Kommentare