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furazan

Dinitro-[di-Furazanyl-Hydrazine]

This compound has a structure of $(\text{NO}_2)(\text{C}_2\text{N}_2\text{O})\text{NHNH}(\text{C}_2\text{N}_2\text{O})(\text{NO}_2)$, where $(\text{C}_2\text{N}_2\text{O})$ is a furazan ring. It is also known as dinitrohydrazofurazan. This compound probably has a power between RDX and HMX, with a lower sensitivity. The gas products from decomposition would be hotter than that from RDX, but the compound is probably less energetic than the nitramines. The linking hydrazine group may make the compound less chemically and thermally stable than the nitramines, although since the hydrazine is electron donating, it will be less susceptible to oxidation than otherwise. The furazan rings do not lend themselves to aromaticity, so the extent of the hydrazine stabilizing the molecule through electron donation will be severely curtailed. The presence of the hydrazine will allow molecules to pack closer together through hydrogen bonding, the hydrazine also serving to link together two nitrofurazan groups, giving a higher density than the nitramines.

3,3-diamino,4,4-azoxy furazan, which has a structure of $\text{NH}_2(\text{C}_2\text{N}_2\text{O})\text{N}=\text{N}(\text{--O})(\text{C}_2\text{N}_2\text{O})\text{NH}_2$ has a det. velocity of 8020 m/s, while the same compound, except with a central azo ($\text{--N}=\text{N--}$) instead of an azoxy group has a det. velocity of 7600 m/s.

Synthesis:

To 25mL ethanol in a 100mL round bottomed flask, 0.013g (0.00022 moles) glacial acetic acid was added. To this was added 0.05g (0.0002 moles) DinitroAzoFuroxan, and 0.5g iron wire (Zn powder may substitute). This is stirred at relaxed for one hour, then 25mL water and about 1g sodium bicarbonate was added. This was extracted with three 20mL allotments of methylene chloride CH_2Cl_2 . The extracts were washed twice with water and the resulting solution was then dried with anhydrous MgSO_4 and filtered. The solvent was removed to leave yellow crystals, which had a melting point over a 160-171degC transition. The compound exothermically decomposes at 215C. If heated rapidly 12deg beyond this, it detonates.

DinitroAzoFurozan Precursor:

In a 250mL round bottomed flask, 0.40g AminoNitroFurazan was dissolved in 16mL concentrated HCl (0.53mol). 0.95g (0.006mol) Potassium permanganate was dissolved in 105mL water. The acid solution in the round bottomed flask was heated to 40degC, then the permanganate solution was slowly dripped into the round botomed flask, over the period of 1 hour. The resulting dark brown solution was heated to a little under 57degC for 2 hours with continued stirring. The solution was cooled, then it was extracted with four 50mL allotments of methylene chloride. The extracts were washed with water, then dried with anhydrous MgSO_4 and filtered. The remaining solution was evaporated under reduced pressure until an orange oily liquid remained, which contains Diamino di-Furazanyl-Hydrazine; to crystallize the compound out, it must be repeatedly dried with organic solvent and evaporated, and finally be chilled.

AminoNitroFurazan

100mL flask placed in ice bath and constantly stirred, 56mL 50% H_2O_2 solution (0.97mol) was added, keeping temperature under 5degC. 5g of sodium tungstate Na_2WO_4 was added, 1.1g of DiaminoFurazan was added and allowed to react for 12 hours. The resulting yellow solution was neutralized with sodium carbonate until neutral pH was reached. The solution was filtered and extracted, similar to the procedures described above. Yellow Crystals were obtained on evaporation, melting over 120-125degC, with explosion at 170degC.

These are tested procedures, however a theoretical shortcut would be to bubble a limited quantity of NO_2 into the furazan of ethylene, giving mono-nitrofurazan, which has a significantly lower vapor pressure than the original reactant, then addition of chlorine will make nitro,chloro furoxan. This will condense with symmetric diacetyl hydrazine, and this will slowly hydrolyze in hydrazine hydrate to form Dinitro-[di-Furazanyl-Hydrazine]. Diacetyl hydrazine can be made by treating concentrated N_2H_4 with Ac_2O , no unsymmetric diacetyl hydrazine will be produced. Note that both nitrogen dioxide and chlorine react at room temperature with the furazan of ethylene, since double bonds exist on the carbon.

As a sidenote,

In the case with plain ethylene, the reaction with nitrogen dioxide is almost entirely the addition of two nitro groups, breaking the double bond. The reaction of NO_2 with the 2-hydroxy propylene (tautomer of acetone) is entirely the oxidation of one of the hydrogens, conserving the double bond.

Other Furazans and Furoxans

See the attachment below for DiaminoFurazan Synthesis

For a related compound, see <http://en.wikipedia.org/wiki/4,4%E2%80%99-Dinitro-3,3%E2%80%99-diazenofuroxan>

Dinitroazofuroxan (formula $\text{C}_4\text{N}_8\text{O}_8$) is thermally unstable, has a detonation pressure of 460kbar, and a detonation velocity of 9.7 km/sec at 1.94 g/cm³.

Dinitroazofurazan, $\text{O}_2\text{N}(\text{C}_2\text{N}_2\text{O})\text{N}=\text{N}(\text{C}_2\text{N}_2\text{O})\text{NO}_2$, has a melting point of 56degC, and a density of 1.73g/cm³, with an observed heat of formation of 168.4 kcal/mol. heat of combustion: 2.125 kcal/g

Dinitroazoxyfurazan, $\text{O}_2\text{N}(\text{C}_2\text{N}_2\text{O})\text{N}[\text{+}](\text{--O}[\text{-}])=\text{N}(\text{C}_2\text{N}_2\text{O})\text{NO}_2$, has a melting point of 112degC, and a density of 1.82g/cm³, with an observed heat of formation of 154.7 kcal/mol. heat of combustion: 1.952 kcal/g

The $\text{--N}=\text{N--}$ can be oxidized to azoxy $\text{--N}=\text{N}(\text{O})\text{--}$ using ammonium persulfate with oleum (conc H_2SO_4 enriched with SO_3) between 80-90degC.

4,4'-diamino-3,3'-azofuroxan has the structure $\text{NH}_2(\text{C}_2\text{N}_2\text{O}_2)\text{N}=\text{N}(\text{C}_2\text{N}_2\text{O}_2)\text{NH}_2$.

Kommentare