nitrocubane

Because of the high degree of complexity of the complete synthesis, details of the procedure have been omitted, the below is merely an overview.

Nitration of Cubane

1,3,5,7-tetranitrocubane (C8H8(NO2)4) is the first nitrocubane that will be looked at. TNC is synthesised from cubanecarboxylic acid chloride (cubylmethanoyl chloride).

TNC is remarkably kinetically stable, just like cubane, surviving hammer blows without reaction, which is quite extraordinary for an HEDM. It also decomposes, rather than detonating, when melted. It is an extremely dense (1.814g cm^{-3}) crystalline solid.

A little known method, known as *Interfacial Nitration*, can be used to further nitrate TNC. In this procedure, a solution of a salt containing the anion which is to be nitrated is first frozen into a solid fusion (sometimes called a "glass" state). Then solid N_2O_4 is deposited on the surface of the glass. When the glass is allowed to melt, the anion is becomes nitrated. This is a very unusual and inexplicable reaction. Interestingly, the anion, mixed with solid N_2O_4 in the same solvent at just above the solvent's melting point will not react. Despite the unusualness of the reaction, it is very useful, giving good results.

This method allowed the synthesis of two more cubanes - 1,2,3 5,7-pentanitrocubane (PNC) and 1,2,3,4,5,7-hexanitro-cubane (HNC). Both of these compounds are stable, crystalline solids, and very dense (PNC has a density of 1.96 gcm^{-3} at 21^oC), which is an a desirable property for explosives. PNC, like TNC, is stable under ordinary conditions, and decomposes above 250^oC without detonation, like most other cubanes. HNC, however, is difficult to isolate, as it cannot be purified by recrystallisation or solvent extraction, owing to its instability in alcohols. It is therefore very difficult to know exactly what its qualities are, as they could be affected by the solvent (normally ethanenitrile, CH3CN). It also seems to be a typical cubane. Both of these compounds are more acidic than TNC. PNC is 1000 times more acidic than TNC, and HNC even more so. This is probably caused by the highly electronegative nitro-groups pulling electron density out of the cubane system, weakening the C-H bonds.

However, *Interfacial Nitration* proved somewhat inadequate, as it could only produce hexanitro cubane (with no more than six nitro groups). Another method needs to be utilized to add more nitro-groups.

Heptanitrocubane

The formation of heptanitrocubane (HpNC) can be achieved by adding four equivalents of $NaN(TMS)_2$ to TNC in a 1:1 THF:2-methyl THF at -78^oC. This is then then chilled to -125^oC, and excess N_2O_4 in cold 2-methylbutane added. The reaction is allowed to proceed for one minute, before being quenched with nitric acid in cold ethoxyethane. This is then added to water, and gives HpNC in high yield. However, this method, unexplainably, proved unable to nitrate the 8th carbon. A new reaction had to be found before octanitrocubane could finally be synthesized. It should also be noted that the C8(NO2)7(-) anion cannot be nitrated by a nitronium NO2(+) ion.

HpNC is a white, crystalline solid which is unusually dense (2.028 g/cm^3) for a compound that consists only of carbon, hydrogen, nitrogen, and oxygen. It decomposes, without detonation, at above 200^oC. It is a moderately strong acid - it protonates liquid methanol to give $CH3OH2^+$. However, it is also unstable under alkaline conditions; even NaF in methanol will catalyse its decomposition. HpNC decomposes very violently, although without actual detonation, in the presence of pyridine.

Octanitrocubane

The eventual explanation for the non-formation of octanitrocubane was the fact that the heptanitrocubyl anion is too stable to react with N_2O_4. This led to the treatment of the heptanitrocubyl anion with the much stronger oxidants, such as NOCl. The reaction of heptanitrocubyl lithium with excess NOCl in CH_2Cl_2 at -78^oC, followed by ozonation, gives octanitrocubane in an approximately 50% yield.

Octanitrocubane(ONC) is a white crystalline solid which sublimes at 200degC. It is fairly thermally stable, the decomposition temperature is well above 200^oC, and there is no observable decomposition even up to 220 ºC. The compound survives hammer taps, and seems to be able to be stored for long periods - samples have survived unchanged for over a year. It has been reported as fairly resistant to mechanical impact. However, recent testing has revealed that ONC has somewhat lower explosive performance than predicted and is more sensitive to impact than first reported.

ONC has an observed density of 1.979g cm^{-3}, which, although very high for a nitrated organic molecule, is still lower than expected - indeed, it is lower than the density of HpNC! This dissappointing observation casts some doubt on the compounds potential as a useful explosive.
However, nitro compounds often have different polymorphs (different crystal packing arrangements,) which have different densities. For example, CL-20 has several polymorphs, with densities ranging between 1.91 to 2.044g cm^{-3}. It is quite possible that ONC could not have other, as yet unobserved or unpublished, polymorphs with higher densities. Polymorphs are often difficult to find - the only way to see if there are other polymorphs would be to crystallise ONC from different solvents at different temperatures, and see if the solids produced have different densities. This is a very time consuming process. Predictions state that the most dense polymorph of ONC would have a density of above 2.1g cm^{-3}, which is considered very high.

The greatest obstacle to ONC finding any useful application is the complexity of preparation and, relatedly, the cost of production. Cubane itself is extremely expensive. Unless the price of cubane drops, cubane based explosives are unlikely to be used commercially or militarily.
On the other hand, if the price of cubane were to be extremely reduced in the future, then TNC or HpNC might be favored for use more than ONC, as they would then be less expensive and, in the latter case, likely denser than ONC.

Performance Comparison to Other Common Explosives

	Density g/cm3	DetonationVelocity km/sec	DetonationPressure kbar
TNT	1.6	7.0	190
RDX	1.8	8.8	338
HMX	1.9	9.1	390
HNB	2.0	9.4	406
CL-20	2.0	9.4	420
ONC	2.1	10.1	489 *predicted*

Although it has one less nitro group, heptanitrocubane has a higher observed detonation velocity than the current observations for ONC.

Preparation of Cubane

In 1966 J C Barborak discovered a new synthesis of cubane. It was slightly unconventional in the fact that it utilized cyclobutadiene as a key substance to the process. Before this, cyclobutadiene was usually unavailable for the purposes of organic chemistry due to it's instability. A new method, using a Barton decarboxylation reaction, gives increased yields of the final cubane product.
t-BuSH stands for tributyltin hydride, which has a high toxicity. Unfortunately, tris(trimethylsilyl)silane, which is usually used as a safer substitute, does not have quite as much affinity for sulfur atoms.

Kommentare

Sie sind nicht berechtigt, Kommentare hinzuzufügen.