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Hexanitrostilbene and Its Properties

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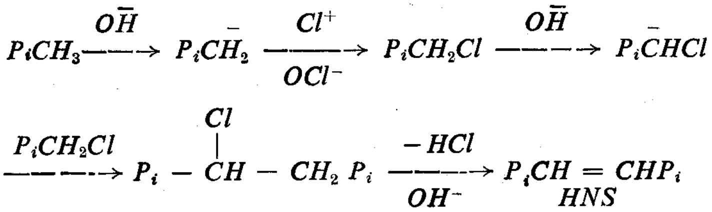
Abstract. 2, 2′, 4, 4′, 6, 6′ hexanitrostilbene (HNS) is one of the prominent heat resistant explosives which can withstand temperature upto 325°C. This has been widely used in space programmes and in aerospace devices. A survey on the progress made so far in the field of its production, evaluation and uses has been compiled.

1. Introduction

With the advancement in the field of aerospace devices and in space shuttle programme, thermally stable (heat resistant) explosives have been used with a great degree of reliability under high temperature conditions. Among the few known heat resistant explosives, HNS is one of the important explosives which is practically insensitive to electrostatic spark, less sensitive to impact than tetryl, radiation resistant and is only commercially available explosive which[1] meets the explosive sensitivity requirement of the fuze design safety criteria of all the three services. It[2] can withstand temperatures upto 325°C. Apollo 17 mission utilised plastic bonded explosives[3-4] composed of HNS and teflon in seismic charges which have got excellent thermal stability at elevated temperature, superior resistance to sublimation at high temperature and low pressure. In addition, HNS is finding applications[5] in mild detonating fuse (MDF), in shielded detonating train (SDT) and in aluminium sheathed linear shaped charges (ALSC). It[6] also improves the crystallization pattern of TNT.

2. Synthesis

About seventy years ago, Reich[7] *et al.* reported a product (m.p. 211°C) assuming it to be 2, 2′, 4, 4′, 6, 6′ hexanitrostilbene, which they obtained by reaction of trinitrobenzyl bromide with alcoholic potassium hydroxide. Later on when this procedure was repeated by shipp[8], a different product (m.p 316°C) was obtained which was really 2, 2′, 4, 4′, 6, 6′, hexanitrostilbene and this was confirmed through infrared spectra and elemental analysis. It was also found that the compound reported by Reich *et al* was 2, 2′, 4, 4′, 6, 6′, hexanitrobibenzyl. Shipp and Kaplan[9] further carried out exhaustive study about its formation and put forward two mechanisms. In first mechanism they supposed the displacement-elimination reaction as given below :

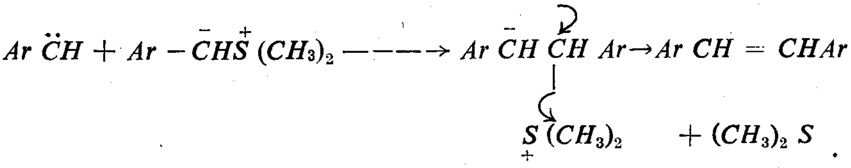


$$P_iCH_3 \xrightarrow{O\bar{H}} P_i\bar{C}H_2 \xrightarrow[OCl^-]{Cl^+} P_iCH_2Cl \xrightarrow{O\bar{H}} P_i\bar{C}HCl$$

$$\xrightarrow{P_iCH_2Cl} P_i - \overset{\overset{\displaystyle Cl}{|}}{C}H - CH_2\,P_i \xrightarrow[OH^-]{-HCl} \underset{HNS}{P_iCH = CHP_i}$$

$(P_i = 2, 4, 6 -$ trinitrophenyl$)$

In the second mechanism they thought some intermediate trinitrophenyl methylene was formed as reported by Hanna *et al*[10]. in the case of 4 nitrobenzyl chloride which formed 4 nitrophenyl methylene as intermediate when reacted with alkali to yield 4, 4′, dinitrostilbene. Swain and Thornton[11] also suggested the formation of the stilbene via the intermediacy of 4 nitrophenyl methylene which then adds to 4 nitrobenzyl dimethyl sulphonium ion to yield 4, 4′, dinitrostilbene as depicted below :



$$Ar\,\ddot{C}H + Ar - \overset{-}{C}H\overset{+}{S}(CH_3)_2 \longrightarrow Ar\,\overset{-}{C}H\,\underset{\underset{\overset{+}{S}(CH_3)_2}{|}}{C}H\,Ar \rightarrow Ar\,CH = CHAr + (CH_3)_2\,S$$

$(Ar = 4$ nitrophenyl$)$

But Shipp *et al.* favoured the displacement elimination mechanism which is supported by the results of reactions, in which the molecular ratios of alkali to trinitrobenzyl-chloride were varied while other conditions were maintained constant in the synthesis of HNS. The reaction revealed that concentration of alkali had pronounced effect on the yield of HNS. The maximum yield of stilbene was found when the mole ratio of alkali to chloride is 1:1 as shown in the Table 1.

Table 1. Effect of concentration of alkali on the yield of HNS

Mole ratio of chloride to NaoH	Yield (%)
1:0.25	11
1:0.50	25
1:0.75	40
1:1.00	50
1:1.50	25
1:2:00	0

Sodium hypochlorite, calcium hypochlorite or potasium hypochlorite in concentrations varying from 5-12% were used in the synthesis of HNS and 42% yield was obtained. Procedures for the preparation of 2,4,6 trinitrobenzyl chloride with 85% yield and 2, 2′, 4, 4′, 6, 6′ hexanitrobibenzyl with 79% yield were reported.

Later on three modifications of Shipp process[9] were reported as depicted in Figs. 1 to 4.

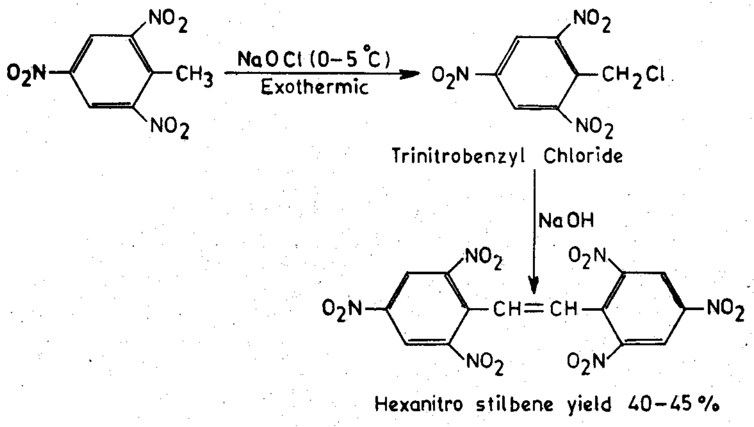


Figure 1. Shipp process[9].

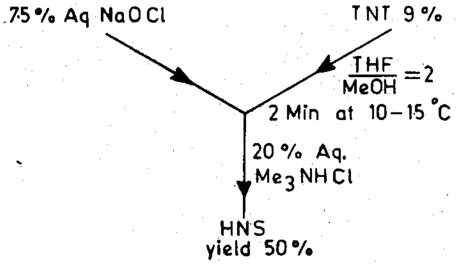


Figure 2. U. K. Lab. Process[13].

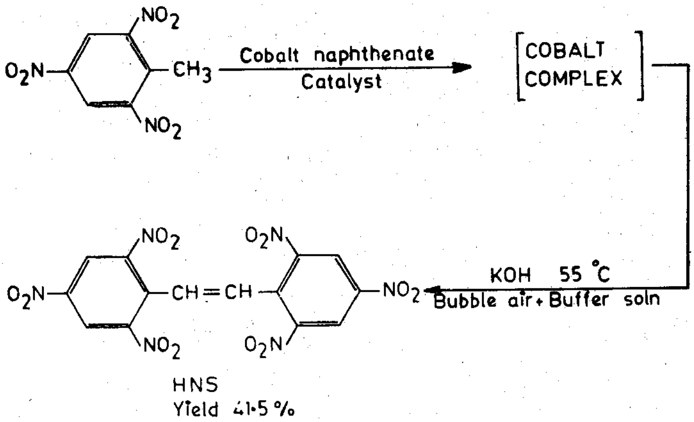


Figure 3. Kompolthy-Hungarian process[14].

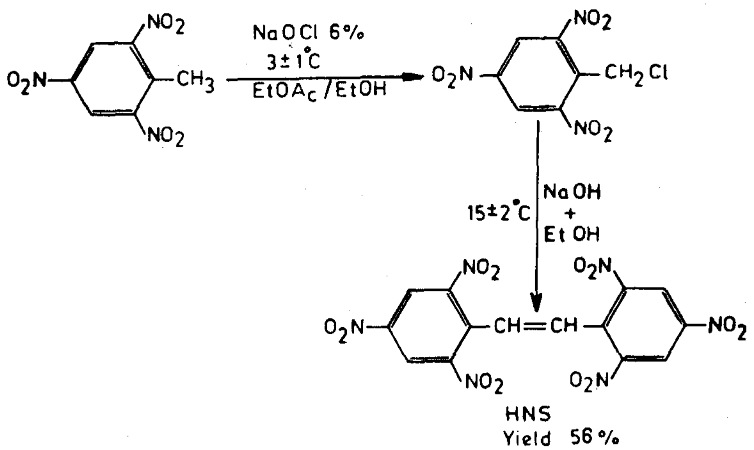


Figure 4. TBRL process[12].

A continuous process[15] for synthesis of high purity HNS was reported with 38% yield. Optimum reaction conditions were studied in which washing and slurrying procedures were developed to yield high purity HNS.

Some variations[16] in the Hungarian process for the manufacture of HNS were carried out but there was no improvement in the yield of HNS.

A new procedure[17] with high yield was reported in which 2,4,6, trinitrobenzylchloride and $NaoH$ were interacted in the organic solvent-water (2 phase system) alongwith triethylbenzyl ammonium chloride as a catalyst.

The synthesis of HNS was studied[18] by oxidative coupling of TNT with Co (II) naphthenate, $CuSO_4$ pyridine mixts, $FeCl_3$, $Co\ (NO_3)_2\ 6H_2O$, MnO_2 and its mixtures with $CuSO_4$ and pyridine, etc. The effect of base concentration and temperature on the synthesis and the reaction mechanism was discussed. One more continuous[19] process was reported for the synthesis of HNS from TNT in which recrystallisation was done in Conc HNO_3 which has sufficient thermal stability at 260 with deflagration at 330°C. Mixtures with 5% poly tetrafluorethylene, deflagrated at 342° and had 6900 m/s detonation velocity. Procedure[20,21] for converting hexanitrobibenzyl into HNS were patented in which 2, 2′, 4, 4′, 6, 6′ hexanitrobibenzyl was treated with tetramine copper sulphate in a solvent like DMF with stirring at 50°C, poured into water, acidified with HCl and filtered and dried to give more than 65% yield of HNS. One more method[22] of synthesis of HNS from HNBB (hexanitrobibenzyl) was reported with high yield (83%). In this HNBB was reacted with bromine in the presence of pyridine while stirring. It was mixed with water and filtered; it was purified with acetone to get HNS. Recently Gilbert[23,24] synthesised HNS from TNT in two stages. In first phase TNT was converted into 2, 2′, 4, 4′, 6, 6′, hexanitrobenzyl, in the second phase hexanitrobibenzyl was transformed into hexanitrostilbene. He made exhaustive study on the synthesis by (i) employing cheaper solvent systems replacing the toxic and expensive solvent system. (ii) by optimizing reaction parameters, such as reaction temperature, amount of reagent and quantities of solvents. (iii) obtained the yield of HNBB upto 82%.

In the 2nd step the HNBB is oxidized by following various systems and yield of HNS was obtained upto 92%.

(i) Copper compounds

(ii) haxogenating agents

(iii) air or oxygen preferably with the addition of promoters

(iv) Quinones

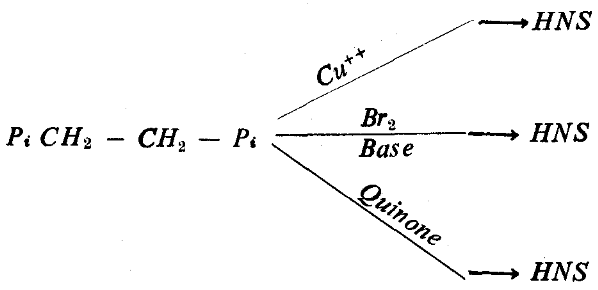
(v) Various oxidizing agent like CrO_3, $FeCl_3$, MnO_2, H_2O_2 Mechanism involved in the reactions are given below :

$$\underset{TNT}{2\ P_i\ CH_3} \xrightarrow{[0]} \underset{HNBB}{P_i\ CH_2 - CH_2\ P_i} \xrightarrow{[0]} \underset{HNS}{Pi\ CH = CH\ P_i}$$

$$2\ P_i\ CH_3 \xrightarrow{O\bar{H}} 2\ P_i\ \overset{--}{CH_2}$$

$$P_i\ \overset{--}{CH_2} + Cl^+ \longrightarrow P_i\ CH_2\ Cl$$

$$P_i\ \overset{--}{CH_2} + P_i\ CH_2Cl \longrightarrow P_i\ CH_2CH_2\ P_i + \bar{Cl}$$



(P_i = 2, 4, 6 trinitrophenyl)

Sandoval[25,26] has scaled up the process for the synthesis of HNS to 5 Kg quantities via intermediate dipicryl ethane in which intermediate was prepared by Shipp process and converted to HNS by Hungarian procedure.

One more method[27] was patented for the preparation of HNS in which it is produced by the reaction of TNT with an alkali metal, or alkaline earth metal hypochlorite in the presence of alk-earth metal oxide, hydroxide or carbonate in aq. organic solvent.

Purification

The products obtained by synthesis are generally crude and impure. To eliminate the undesirable byproducts, different methods were adopted as given below :

(i) Solvent method

(ii) Chemical method

Crude HNS was purified with solvents like acetone, benzene or DMF. The comparative low solubility of HNS over the impurities in the organic solvents had been made use of for its separation. It was further purified by repeated recrystallization in DMF or nitrobenzene.

A chemical method also had been reported[12] in which crude HNS was refluxed in nitric acid (55%) which decomposes the impurities.

Detection and Separation

In the synthesis of HNS from Shipp process it was observed that HNS was contaminated with hexanitrobibenzyl (HNBB), trinitrobenzyl chloride, TNT, TNB, trinitrobenzylalcohol etc., An analytical method had been developed at NAVSWC (Naval Surface Weapon Centre) to characterise these impurities both qualitatively and quantitatively.

Several impurities resulting in the preparation of HNS as well as HNS itself can be detected[13-28] by High Pressure Liquid Chromatography (HPLC).

A X-ray diffraction method[9] is also reported in which HNS can even be identified in polycrystalline samples.

An improved method[30] for analysis of HNS by liquid chromatography is reported in which a μ Bendapak NH_2 Column was used. A procedure[31] was developed for the compositional analysis of plastic bonded explosive containing HNS.

3. Polymorphs Of HNS

HNS I exists as thin plate and is very fluffy. This geometry is not desirable as it has got very poor crystalline flow. Taylor and Osterling[13] developed a method in which HNS was processed in organic solvent system comprising of acetonitrile and toluene. Larger particles of HNS of rectangular shape were obtained. It was named as HNSII. It has higher density than HNS I. The process was incapable of providing significant yield of HNS II so it was not suitable commercially (Table 2).

Syrop L. J.[32] further improved the process by patenting new apparatus as well as taking new solvent system, viz. a acetonitrile/xylene which do not form azeotropic mixture like acetonitrile/toluene. In this process, denser, coarser and orthorhombic shape crystals of HNS II were obtained, which has got free flowing property.

Table 2. Comparative Properties[35] of HNS I and HNS II

	Type I	Type II
Shape of the crystal	Fluffy thin plate	Dense orthorhombic
Melting Point, °C	316 (dec)	319 (dec)
,, °F	601 (dec)	607 (dec)
Particle size, mlcrons	1—5	100—300
Bulk density, g/cc	0.32—0.45	0.45—1.0
Differential thermalanalysis on set of exotherm	315°C (599°F)	325°C (617°F)
Electrostatic spark sensitivity, fires above ufd	0.001@ 8 kv	0.0001 @ 17 kv
Friction sensitivity 10/10 No fires	440 kg/cm	440 kg/cm
Impact sensitivity 50% height, cm NOL-ERL Machine Type 12 tools 5/0 Sandpaper 2.5 kg wt.	44	61
Vacuum stability @ 260°C 1st 20 mins, cc/g/hr	1.8	0.3
Addnl 2 hrs, cc/g/hr	0.6	0.2
@ 280°	2.7	2.7
Velocity of deton, m/sec	7000	7000
density, g/cc	1.70	1.70
Autoignition point	325°C. (618°F)	325°C (618°F)
Decomposition rate @ 260°C	0.1%/hr	0,1%/hr
Heat of combustion, cal/g	3451	3451
Mean firing voltage for EBW, 1 µfd capacitor	12950@ 0.9g/cm^3	12950@ 0.9g/cm^3
Vapour pressure	2.9x10^{-8}mmHg @16°0C (320°F)	2.9x10^{-8}mmHg @160°C (320°F)

Another process for obtaining HNSII was reported[33,34] in which HNSI was dissolved in hot DMF, filtered and further subjected to heating and cooling cycle. After cooling the slurry was washed with acetone and dried.

Fine Grade HNS

Recently a method[36] was patented for getting fine crystals of HNS, by dissolving HNSII in hot fuming nitric acid and drowning in ice cold water.

A process[59] for producing fine particle size HNSI was reported in which HNS was disolved in DMF and this solution was slowly added into a pre-cooled, rapidly agitated distilled water and the resulting material was filtered, washed with acetone/water and freeze-dried. It has been noticed that HNS which has been processed/recrystallised through organic solvent method has better thermal stability than the material recrystallised from nitric acid.

Stability of HNS

Kilmer[37] has tested the thermal stability of HNS recrystallised from acid or organic solvents in silver and aluminium detonating cords. Gould[38] determined the thermal stability of HNS by measuring the detonation velocity precisely of samples exposed to 20, 150, 175, 200 and 225°C. Sandoval[39] studied the effect of dipicrylethane which is a common impurity in HNS on the volatiles, evolved during the vacuum stability measurement.

4. Thermal Decomposition/Nuclear Radiation Damage

HNS was subjected[40] to neutron and gamma radiation from a power reactor at flux levels of about $3.85 \times 10^8 r$ per hour and 7.5×10^{12} neutrons/cm^2/sec. fast neutron flux, unchanged compound remaining after irradiation was determined by thin layer chromatography. Similar samples heated at 280°C were analysed for residual compound (Table 3). Ratios of unchanged samples to solid products proved nearly the same for irradiated and heated samples at each of three levels of degradation for corresponding equivalent weight losses.

Properties of HNS

HNS (m.p : 316° C) is a yellow crystalline substance. It exists in two forms HNSI and HNSII. It is relatively insoluble in the solvents. Its solubility[12] in various organic solvents has been given in Table 4 and other properties[41] are compared in Table 5.

Charge Transfer Complexes of 2, 2′, 4, 4′, 6, 6′ *Hexanitrostilbene* (*HNS*)

Several charge transfer complexes of HNS were prepared[42,43] from aniline and its derivatives, toluidine and their derivatives anisidine, 1-naphthalamine, etc. isoquinoline etc. The majority of these complexes contain two molecules of the complex forming compound per mole of HNS. These complexes may be useful in the identification and separation of HNS.

Table 3. Effect of nuclear radiation/heat on HNS

Time of Irradiation (min.)	HNS	Solid product (by difference)	Weight loss (gaseous products) (%)
120	86	12	2.2
180	69	27	3.8
240	54	40	5.8
Time of heating at 280° C			
319	93	5	2.02
462	74	22	3.8
554	52	42	5.8

Table 4 Solubility[12] of HNS (g/100 ml of solvents) at various temperature in °C

Solvent	30	40	60
Nitrobenzene	0.059	0.072	0.094
Ethyl-methylketone	0.035	0.052	0.061
Acetone	0.064	0.075	0.131
Methanol	0.003	0.006	0.008
Dimethylformamide	1.312	1.703	2.198
Acetonitrile	0.043	0.064	0.084
Cyclohexanone	0.118	0.156	0.206

Table 5 Comparative properties[41] of some explosives

	HNS II	HMX	HNAB	PETN
Colour	yellow-buff	White	Orange	White
Max theoretical Density (g/cm^3)	1.74	1.90	1.76	1.77
Bulk density (g/cm^3)	0.36	0.66	0.64	0.29
Melting point (°C)	318	285	220	140
Specific heat (cal/g/°C)	—	0,28	—	—
Vapour pressure at 100°C (mm Hg)	1×10^{-9}	3×10^{-9}	1×10^{-7}	8×10^{-5}
Linear coefficient of thermal expansion (cm/cm/°C)	9.2×10^{-5}	5.0×10^{-5}	8.0×10^{-5}	11.3×10^{-5}
Resistivity[14] (ohm-cm)	5×10^{13}	4×10^{10}	–	3×10^{12}
Dielectric strength (volts/mil)	400	90	–	130
Heat of explosion (cal/g)	958	1360	1030	1380
(kj/g)	4.0	5.7	4.3	5.8
Volume of detonation gases at STP (cm^3/g)	756	908	780	780

Compatibility of HNS with RDX

The study[44] of compatibility was reported in which a pellet of RDX was sandwitched between two HNS pellets which were placed in container in helium atmosphere and aged at 60° and 100°C.

Effect of HNS on Physical Properties of TNT

Small concentration of HNS were used to modify the grain structure of TNT, when nucleation[45] and growth of TNT containing HNS was investigated using hot stage microscopy, it was revealed that effective nucleating agent was an associated complex of HNS and TNT formed in the molten stage. It was observed[46,47] that nucleant was not HNS which was added originally but a complex $(TNT)_2$ HNS has formed during thermal cycling of the individual components. The preproduction and simple addition of the complex just prior to casting is a feasible alternative to the cycle cast technique currently being employed. The existence of complex of TNT and HNS was confirmed[48] and its presence promotes TNT cast of superior quality.

Plastic Bonded Explosives

Heat stable composition based on vinylidine fluoride, melamine and teflon and HNS were developed[49]. It was observed that mixture has a pressed density and thermal properties closely resembling with the explosive, and its machinability and handling characteristics are also similar. New composition[50] HNS/Teflon (90/10) found use in space programs because of its excellent thermal stability at elevated temperature, superior resistance to sublimation at high temperature and low pressure and ease of molding the powder, pressing and machining. The impact sensitivity is between that of composition B and composition A_3. Under the severe conditions of the moon's surface the explosive successfully performed its intended function of generating seismic waves. It was further observed[51] that detonation properties of HNS/Teflon (90/10) charges were unaffected by the adverse environment. The compressive strength was improved[52] by thermal cycling after fabrication. HNS was proved an excellent explosive in the Appollo mission.

Detonic Properties

It is reported[53] when a series of 0.2 to 0.3 of HNS charges were detonated in vacuum of 10^{-3} and 10^{-5}, form the resultant freely expanding detonation product, gas blast, achieves terminal velocities of 8-12 km/sec within 3-5 μ/sec after the detonation wave arrives at the free surface. Detonation velocity[54] and pressure measurement on 2 lots of HNS explosives HNSI and HNSII were made using aquarium technique and antenna technique. There were no significant difference in the results of the two tests. Computational experiment[55] were performed to determine the threshold pressure sufficient to produce a detonation in HNS. Lee *et al.*[56] carried out extensively experiments to determine the detonation behaviour of HNS at charges densities of 1, 1.2, 1.4, 1.6 and 1.65 g/cm^3. Estimates of equation of state of detonation products were made for each charge density Davies[57] *et al* measured shock sensitivity to initiation of HNSII by plate impact and electron beam technique. Stull[58] had undertaken the study to determine which of the four methods for producing HNSII provides optimum material for processing and use in the aluminium linear shaped charges.

5. Application of HNS

A great deal[41] of data has been gathered on the utilization of hexanitrostilbene (HNS) in explosive components. HNS is one of the new thermally stable explosives which may be subjected to temperature as high as 500°F. The report compares data of HNS with that on other explosives and lists values and graphs for DTA data, compaction properties, detonation velocity vs. density, shock initiation sensitivity, impact sensitivity, hydrocompaction, minimum use diameter, compatibility with other materials, and hazards information.

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