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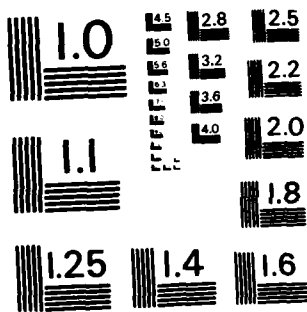
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4,6-DINITROBENZOFUROXAN, AN IMPORTANT EXPLOSIVE
INTERMEDIATE

Robert J. Spear, William P. Norris and Roger W. Read

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4,6-DINITROBENZOFUROXAN, AN IMPORTANT EXPLOSIVE INTERMEDIATE

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ABSTRACT

The preparation of 4,6-dinitrobenzofuroxan (DNBF) from either benzofuroxan or picryl chloride is described. Batches of up to 20 g have been obtained in suitable crystalline form via recrystallisation from a number of solvents. DNBF exhibits impact and electrostatic sensitivity characteristic of a sensitive secondary, such as RDX, and should be handled accordingly. Ignition of small samples (< 200 mg) results only in deflagration; detonation can be achieved by the strong shock from detonating lead azide but power output appears to be significantly lower than RDX.

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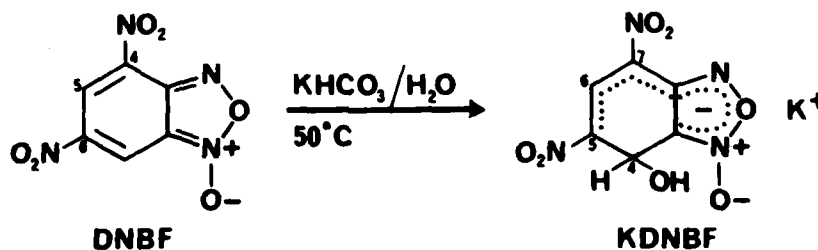


4,6-DINITROBENZOFUROXAN, AN IMPORTANT EXPLOSIVE

INTERMEDIATE

1. INTRODUCTION

In 1899 Drost [1] reported that nitration of "o-dinitrosobenzene", first prepared in 1892 [2], gave a dinitro derivative. The structure of these so-called "o-dinitrosobenzenes" remained a source of controversy till as recently as 1950 when the benzofuroxan structure was firmly established [3]. The structure of Drost's dinitro derivative [1] was thus 4,6-dinitrobenzofuroxan (DNBF)*, later confirmed by x-ray crystallography [4].



DNBF is an explosive [5,6] but the main interest in this compound has been as an intermediate to the explosive salts [1,5] formed via its dissolution in alkaline aqueous bicarbonate solutions. The most important of these is the potassium salt, known in the explosives literature as KDNBF**,

* We have chosen here to retain the name commonly used in the explosives literature. Chemical Abstracts lists DNBF under 4,6-dinitrobenzofurazan 1-oxide.

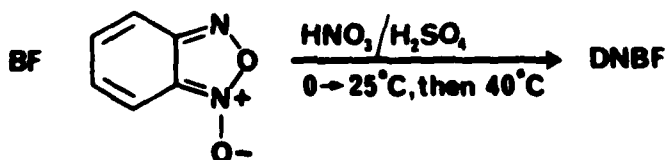
** The name potassium dinitrobenzofuroxan was used in the pre-1970 literature owing to the fact that the structure was not known. The Chemical Abstracts listing for KDNBF is now under potassium 1,4-dihydro-5,7-dinitrobenzofurazan-3-oxide.

which has found use as a primary explosive in initiating compositions [5,7]. As part of our investigations into new improved primary explosive materials, we have been studying the preparation of structural analogues of KDNEF. In these studies we have examined changes in the metal ion (from K^+) [8] and replacement of the OH group at C4 by other functional groups [9,10]. During this continuing work we have prepared and handled relatively large quantities of DNEF. Despite DNEF having been known for over 80 years, the only descriptions we could find of its explosive properties were "This compound is an explosive, ca. 130% as powerful as picric acid, but is too sensitive for use as a high explosive" [5] and "Dinitrodinitrosobenzene is a powerful explosive: it gives a lead block expansion of 360 cm^3 " [6]. Neither statement was referenced. DNEF is not listed in any other modern compilation of explosive materials.

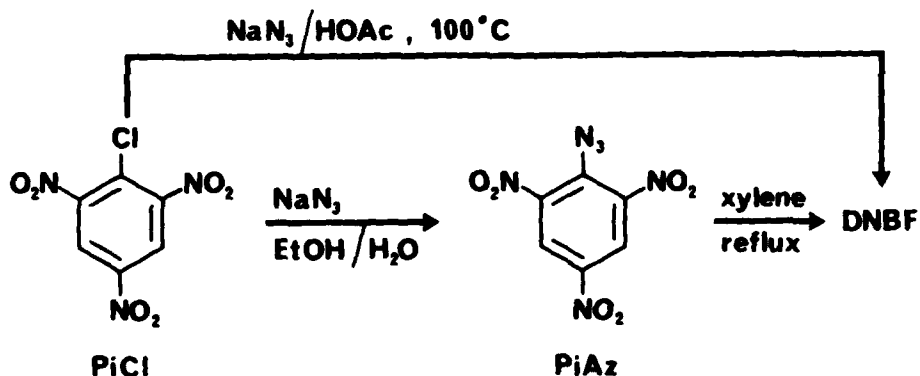
The purpose of the work reported here is twofold. A short first section deals with two (alternative) preparations of DNEF from commercially available materials on a scale suitable for subsequent experimental batch preparations of KDNEF analogues. In the second section the results of standard sensitivity tests and determination of some explosive properties are described. These results serve as an important guide for the safe handling of DNEF in the quantities used for typical batch preparations.

2. PREPARATION OF DNEF

In the majority of studies of DNEF, the authors have used either Drost's original method of preparation [1] or the similar method described by Green and Rowe [11]. Both these methods start with benzofuroxan (BF), a commercially available material, which is nitrated with mixed nitric and sulphuric acids. We have found this method to be simple to perform and to give consistent yields of about 55% after purification. It should be noted that McGuchan [12] has reported in a conference paper that preparation of DNEF by the method of Green and Rowe produces up to 10% of the isomeric 5,6-DNEF, which subsequently interferes with production of KDNEF. We have carefully examined both the crude product from the nitration of BF, and an extract of the filtrate, by FT proton NMR spectroscopy and have found no evidence for the presence of 5,6-DNEF in either. Under these conditions 1% would have been easily detectable.



The major alternative synthesis of DNBf is reaction of picryl chloride (PiCl) with sodium azide, originally reported by Schrader [13]. A major drawback to this method is that the intermediate picryl azide (PiAz) must be isolated then heated under reflux in xylene to give DNBf. PiAz is a powerful explosive more sensitive than tetryl [14] hence it is preferable to avoid isolation of this intermediate. Korczynski and Namyslowski [15] reported in 1924 that heating PiCl and sodium azide in acetic acid at 100°C gave DNBf. Surprisingly their method has not been used in any subsequent investigations of DNBf. In our hands this preparation was extremely easy and reproducibly gave yields of about 80% after purification. Although DNBf did crystallise directly from the acetic acid medium upon cooling, a better isolation procedure was to quench the hot reaction mixture in ice/water, recover the crude product by filtration, then recrystallise.



The method of choice for preparation of DNBf could be either the nitration of BF or the "one-pot" reaction of PiCl with sodium azide. Both reactions are easy to perform and isolation of the product from the reaction medium is straightforward. Although the reaction from PiCl gives a significantly higher yield, the cost of PiCl is over 2.5 times that of BF. Another method of preparation of DNBf which has been reported is the reaction of PiCl with hydroxylamine in the presence of sodium acetate [16]. However, no experimental details were given and we have not further investigated this route.

DNBf readily recrystallises from a range of solvents. In the earlier references [1,11] benzene or acetic acid was used. We have found chloroform, dichloroethane, ethyl acetate or methanol to be suitable. DNBf crystallises from chloroform as small plates while needles are obtained from other solvents.

3. SENSITIVITY TO INITIATION AND EXPLOSIVE PROPERTIES

DNBF was subjected to the standard sensitivity tests: Rotter impact test (F of I, impact sensitivity), electric spark test (sensitivity to electrostatic spark) and T of I test (heat). The results are detailed in Table 1. Although further tests could have been performed, the aim was to generate a measure of the sensitivity relative to known materials rather than an exhaustive testing to diverse stimuli.

The most immediate feature of the data is the impact sensitivity. The F of I, 89, is comparable with that of RDX (80) and tetryl (86) and is significantly higher than that of PETN (51) [17]. This identifies DNBf as a sensitive secondary explosive of the type commonly used as boosters. A similar trend is observed with the data for sensitivity to electric spark where DNBf ignites to explosion at a spark energy of 4.5 J but not 0.45 J. RDX, tetryl and PETN give an identical result.

When subjected to the T of I test, DNBf ignites at about 270°C with fizzing (no explosion) and leaves a black residue. This behaviour can be seen more clearly by hot stage microscopy where melting (173-174.5°C) is accompanied by slow gas evolution. At 210°C gas evolution has ceased but recommences very vigorously at about 235°C. The DSC trace exhibits an endotherm (melting) at 172°C and a strong exotherm commencing at about 245°C.

Explosive properties of DNBf were assessed by preparing a short series of experimental detonators. The results are detailed in Table 2. Entries 1 and 2 were designed to assess ignition properties. In entry 1, ignition from match-head igniter resulted in deflagration only with low power output (minimal damage to the detonator tube) leaving a black residue. Attempted ignition from hot-wire (entry 2) left charring of the sample in the vicinity of the wire but the bulk of the charge remained unreacted.

The remaining two detonators were prepared to check whether DNBf could be induced to detonate. In entry 3, a lead azide/DNBf detonator obviously resulted in detonation of the DNBf as evidenced by the cratering of the witness block. The dent to the witness block was less than a comparable lead azide/RDX detonator which would imply that the power output of DNBf is less than RDX. A lead styphnate/DNBf charge did not result in detonation and unreacted DNBf could be seen adhering to the undented witness block. Obviously the lower power output from lead styphnate is insufficient to induce DNBf to detonation.

4. CONCLUSION

DNBF can be readily synthesised either from benzofuroxan or picryl chloride, both of which are commercially available. The product is obtained as either plates (from chloroform) or needles from solvents such as ethyl acetate or methanol. DNBf exhibits impact and electrostatic sensitivity

comparable with RDX or tetryl and should be handled in a manner appropriate for sensitive secondary or booster explosives. Small charges (< 200 mg), whether unconfined or confined, only ignite to deflagration. DNBF can be induced to detonate by the strong shock from detonating lead azide but not from detonating lead styphnate. The power output upon detonation seems to be less than that from RDX.

5. EXPERIMENTAL

Benzofuroxan (Aldrich), picryl chloride (Tokyo Kasei) and sodium azide (BDH) were all obtained commercially and were used as received. All other reagents and solvents were laboratory grade.

4,6-Dinitrobenzofuroxan (DNBF)

(i) By Nitration of Benzofuroxan

Benzofuroxan (20 g) was dissolved with gentle warming in conc. H_2SO_4 (240 ml) then cooled in ice for 0.5 h. A mixture of conc. HNO_3 (30 ml) and conc. H_2SO_4 (80 ml) was added in portions, keeping the temperature below 25°C. After complete addition the mixture was warmed on a water bath to 40°C, then allowed to stand 5 min. The mixture was poured onto ice and the product isolated by filtration under suction, washed with water and dried under suction; crude yield 20.8 g. Recrystallisation by dissolution in hot chloroform (approx. 600 ml), hot filtration then reduction in volume to 500 ml gave DNBF as yellow-brown plates (14.8 g), mp. 173-4.5°C, lit. [1] mp. 172°C. Reduction of the filtrate to 60 ml gave a second crop of brown crystals (3.3 g), mp. 168-72°C, slightly less pure than the first crop; total yield 54.7%.

(ii) From Picryl Chloride*

Picryl chloride (25 g) and sodium azide (8 g) were added to glacial acetic acid (100 ml) and the mixture heated to 90°C. The deep red solution which evolved nitrogen was heated for 1.5 h then poured onto ice/water (400 ml). The product was isolated by suction filtration, washed with water (250 ml) and dried under suction; crude yield 21.0 g. Dissolution in hot chloroform (900 ml) followed by filtration and reduction of the volume to 600 ml gave, upon cooling, DNBF as yellow-brown plates (14.9 g), mp. 172-4°C. Reduction of the filtrate gave a second crop of brown crystals (3.4 g), mp. 169-72°C, slightly less pure than the first crop; total yield 80.1%.

* This preparation is similar to one communicated to us by Dr. R.L. Atkins, Research Department, Naval Weapons Centre, China Lake, California, USA.

Sensitivity Tests

Impact sensitivity was determined on a Rotter apparatus [17]. Samples of approx. 27 mg were tested using a 5 kg weight falling from heights of 80-200 cm at 10 cm intervals. A total of 50 caps was tested. The figure of insensitivity (F of I) was calculated by comparison with corresponding test results for RDX (F of I 80).

Sensitivity to electrostatic initiation was determined on an instrument built to specification for the Electric Spark Test. Tests were performed at spark energies of 4.5, 0.45 and 0.045 J. Fires/no fires were determined by sound and visual inspection of the sample.

Thermal behaviour was initially studied at a heating rate of 10°C/min using a Leitz Ortholux microscope with an attached Mettler FP-2 hot stage, and subsequently by differential scanning calorimetry (DSC) using a Perkin Elmer DSC-2B. Experimental conditions were vented aluminium pans under a flowing nitrogen atmosphere (15 ml/min), heating rate 10°C/min. Ignition temperatures were determined on an instrument built to specifications for the ERDE T of I test. Samples of 50 mg were heated at 5°C/min and measurements were performed in triplicate.

Investigation of Explosive Properties

Lead azide was type RD1343 and lead styphnate was type RD1303. Both were obtained from MFF St. Mary's, NSW.

Experimental detonators were fired remotely using an 18 V, 0.08 J capacitor discharge firing box which discharged either through a match-head igniter or a platinum bridgewire. The performance of each experimental detonator was assessed by use of an aluminium witness block, with particular importance being placed upon whether a detonation occurred. The dent imparted to a witness block by a detonation has a distinctly cratered appearance with splaying at the edges. The absence of a dent or the presence of a slight indentation which slopes gradually in from the edges indicates that an explosion has occurred but build-up to detonation has not been achieved. Although largely a qualitative test, depth of dent studies have been used to determine detonator performance and a number of experimental variables which affect the depth have been identified [18].

(i) Initiation using Match-head Igniter

Each experimental detonator was prepared by pressing DNB (125 mg) into a flat bottom aluminium ICI detonator tube, 5.57 mm i.d., approximate wall thickness 0.3 mm, using an Eltor press at a pressure of 90.7 MPa. A type E ICI match-head igniter was then crimped into the detonator tube.

(ii) Initiations using Hot-wire

Experimental detonators were prepared from perspex detonator tubes, 4.12 mm i.d., to which had been fitted a bridgewire device using Eastman 910 adhesive. The bridgewire device was constructed of bakelite with copper terminals across which had been spot welded a 0.038 mm diameter platinum wire. A more detailed description can be found in ref. [19]. Explosive charges were prepared by pressing weighed amounts of explosive directly into the detonator tubes at 166 MPa using an Eltor press. Where two increments were used, the initiating charge was pressed in first then the secondary charge was added and pressed on top.

6. ACKNOWLEDGEMENTS

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T A B L E 1

SENSITIVITY TESTING ON DNB

<u>Test</u>	<u>Observation</u>
Impact Sensitivity	
Rotter Impact	F of I 89, cf RDX 80 100% height 170 cm, 0% height 90 cm Mean gas volume 19.75 ml.
Electrostatic Sensitivity	
Electric Spark Test	Fires 4.5 J. No fires 0.45 J.
Thermal Sensitivity	
Hot stage microscopy	Melts 173-174.5°C with slow evolution of gas till ~ 210°C. Gas evolution ceases then recommences about 235°C, very fast.
DSC	Endotherm 172°C, exotherm onset ~ 245°C.
T of I Test	268, 268, 269°C. Rapid decomposition with fizzing, leaves a black residue. 270, 270, 272°C (2nd batch).

T A B L E 2

EXPLOSIVE PROPERTIES OF DNB

<u>Experimental Detonator</u>	<u>Initiation</u>	<u>Observation</u>
1. DNB (125 mg) in aluminium ICI flat bottom tube.	Match-Head igniter	Contents burned leaving black residue.
2. DNB (125 mg) in perspex tube.	Hot-wire	Material around wire charred, remainder unreacted.
3. Lead azide (100 mg) then DNB (100 mg), perspex tube	Hot-wire	Tube destroyed, aluminium witness block cratered.
4. Lead styphnate (100 mg) then DNB (100 mg), perspex tube.	Hot-wire	Tube destroyed, aluminium witness block not dented, unreacted DNB smeared on witness block.

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