

Studies of Stab Initiation. Sensitization of Lead Azide by Energetic Sensitizers*

Robert J. Spear and Paul P. Elischer

Department of Defence, Materials Research Laboratories,
P.O. Box 50, Ascot Vale, Vic. 3032.

Abstract

A series of 17 compounds which ignite and explode upon heating have been synthesized. Ignition temperatures range from 122° to 261°. The ability of these compounds to sensitize the primary explosive lead azide to stab initiation has been determined on 1 : 10 admixtures. The general trend observed was that stab initiation energies increase with sensitizer ignition temperature but the overall correlation is poor. An assessment of the dependence of the ratio of sensitizer to lead azide on stab initiation energies is also included for two of the compounds. The results are interpreted in terms of possible mechanisms for the initiation process and support the hypothesis that frictional processes are of primary importance.

Introduction

Explosives are energetic materials which can be initiated to explosion by a range of mechanical stimulæ: impact,^{1a,1b,2,3} friction^{1c,2,4} and shock.^{2,4,5} One widely used method of mechanical initiation is stab initiation, in which a fast moving needle penetrates a compacted solid explosive charge. The energy imparted to the sample during this process is small (<1 J) and as a result only the very sensitive primary (initiating) explosives are susceptible to stab initiation. Among this class of explosives there is a group of compounds collectively called energetic sensitizers which exhibit moderate sensitivity to stab initiation but which in admixtures with hard primary explosives such as lead azide produce compositions which are extremely sensitive.

The most important energetic sensitizer is the zwitterion form of 1-(1*H*-tetrazol-5-yl)tetraz-1-ene-3-carboximidamide monohydrate ('tetrazene', (1))^{6a,7} which is readily obtained by reaction of aminoguanidinium salts with nitrous acid.^{6a} As an

* Presented in part at the Joint TTCP/JTCG MD, Second Meeting on Explosives, Naval Weapons Centre, China Lake, California, February 24-26, 1981.

¹ Bowden, F. P., and Yoffe, A. D., 'Initiation and Growth of Explosion in Liquids and Solids' (a) Ch. 3; (b) Ch. (4); (c) Ch. 2 (University Press: Cambridge 1952).

² Bowden, F. P., and Yoffe, A. D., 'Fast Reactions in Solids' Ch. 5 (Butterworths: London 1958).

³ Winter, R. E., and Field, J. E., *Proc. R. Soc. London, Ser. A*, 1975, 343, 399.

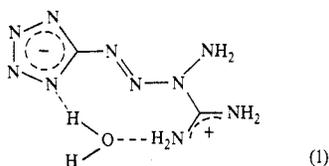
⁴ Fair, H. D., and Walker, R. F., (Eds) 'Energetic Materials' Vol. 1, Chs 8, 9; Vol. 2, Chs 4, 7 (Plenum Press: New York 1977).

⁵ Chaudhri, M. M., *Combust. Flame*, 1972, 19, 419.

⁶ Urbanski, T., 'Chemistry and Technology of Explosives' Vol. 3, Part 2 (a) Ch. 4; (b) Ch. 2 (Pergamon Press: London 1965).

⁷ Duke, J. R. C., *Chem. Commun.*, 1971, 2.

example of the sensitizing action of tetrazene, compacted lead azide requires a stab initiation energy of approximately 1000 mJ but addition of only 2% by weight of tetrazene lowers the required stab initiation energy to about 3 mJ. Practically all percussion primer mixes and stab sensitive mixtures used in percussion and stab sensitive detonators incorporate tetrazene as sensitizing agent. A major drawback to the use of tetrazene in such compositions is its poor thermal and hydrolytic stability, which limits both shelf life and operating conditions under which these stores can be used. As a result there is continuing interest in the development of a stab sensitizing compound which has comparable sensitizing properties to tetrazene but enhanced stability.



The design and selection of new candidate energetic materials with potential stab sensitive or sensitizing properties would obviously be facilitated by a detailed mechanistic knowledge of stab initiation. In contrast to other mechanical initiation methods¹⁻⁵ the mechanism is not well understood despite a number of experimental studies.⁸⁻¹³ The evidence from these studies is consistent with stab initiation being thermal in origin with at least two mechanisms for generation of the thermal 'hot spots'.^{8,9,11,13} A number of experimental variables which directly influence stab sensitivity have been identified. In the case of material properties of the explosive components, both Bird¹² and Chaudhri¹³ have identified the ignition temperature to be important in determining stab sensitivity. In particular, Bird¹² examined a limited number of energetic compounds as binary mixtures (10% by weight) with service lead azide and found a direct correlation between the stab sensitivity of the mixture and the ignition temperature of the energetic sensitizer. Bird also suggested that the sensitizing action of tetrazene results primarily from its low ignition temperature.¹² Other material properties such as hardness and friction coefficient have also been shown to be important, particularly for non-energetic materials such as grits which can also sensitize primary explosives to stab initiation.^{1,2,4,12}

At MRL we are currently engaged in a detailed study of the relationship between chemical and physical properties of explosive materials and their susceptibility to

⁸ Bowden, F. P., and Yuill, A. M., *Nature (London)*, 1953, **172**, 378.

⁹ Forsyth, A. C., Ling, R. C., and Kaufman, J. V. R., Technical Report 2680 (1970), Picatinny Arsenal, Dover, N.J., U.S.A. [Microfiche AD 316883]; Ling, R. C., Forsyth, A. C., Maldonado, J. H., Hayes, L., and Dean, J. F., Technical Report 2404 (1957), Picatinny Arsenal, Dover, N.J., U.S.A. [Microfiche AD 132845].

¹⁰ Voreck, W. E., and Dalrymple, E. W., Technical Report 4263 (1972), Picatinny Arsenal, Dover, N.J., U.S.A.

¹¹ Chaudhri, M. M., Field, J. E., Hagan, J. T., and Coley, M., Proc. 11th Int. Congr. on High-speed Photography (Ed. P. J. Rolls), p. 448 (Chapman & Hall: London 1974); Field, J. E., Chaudhri, M. M., Winter, R. E., Brown, C., and Patel, R., EMR Tech. Rep., August 1974, AT/2029/090/RAR, Cavendish Laboratory, Cambridge, U.K.

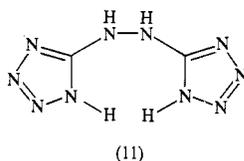
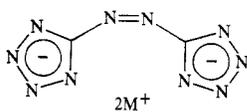
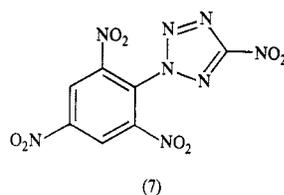
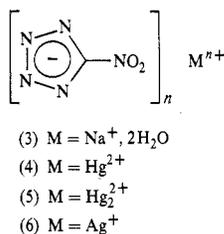
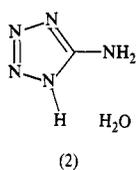
¹² Bird, R., Technical Note No. 362 (1975), Materials Research Laboratories, Maribyrnong, Vic.

¹³ Chaudhri, M. M., *Nature (London)*, 1976, **263**, 121.

stab initiation. We report here, as the first part of this study, an investigation of the relationship between the ignition temperature of an energetic material and its ability to sensitize primary explosives to stab initiation. The hard primary explosive lead azide has been chosen as the substrate for assessment of sensitizing properties.

Results

Our initial experimental approach has been to select a number of compounds which have been reported in the literature to have ignition temperatures between 120° and 200°. We subsequently synthesized these, plus related materials, to give a series of 17 compounds [including (1)] with ignition temperatures ranging from 122° to 261°. This series was largely based on structurally similar compounds derived synthetically from common precursors.



1H-Tetrazol-5-amine monohydrate (2) was converted into sodium 5-nitrotetrazolate dihydrate (3)* by diazotization in the presence of excess nitrite according to the method of Gilligan and Kamlet.¹⁵ Compound (3) was used as an intermediate for the preparation of the desired mercuric (4), mercurous (5) and silver (6) salts¹⁴ by reaction with the corresponding metal nitrates. Dehydration of (3) to the anhydrate, followed by reaction with picryl chloride in dry acetone, afforded a single compound tentatively identified as 5-nitro-2-picryltetrazole (7). Tetrazolate anions with electronegative substituents at C5 undergo preferential substitution at N2 rather than N1¹⁶ and there was no detectable trace of a second isomer in the ¹H n.m.r. spectrum of either crude or purified (7).

* Compound (3) was originally claimed to be a tetrahydrate.¹⁴ Although the hydration state is variable, the product which crystallizes from acetone is the dihydrate.¹⁵

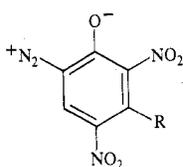
¹⁴ Jenkins, J. M., and White, J. R., Technical Note No. 21 (1970), Explosives Research and Development Establishment, Waltham Abbey, Essex, U.K.

¹⁵ Gilligan, W. H., and Kamlet, M. J., Technical Report 76-146 (1976), Naval Surface Weapons Centre, White Oak Labs, Silver Spring, Md, U.S.A. [Microfiche AD A036 086].

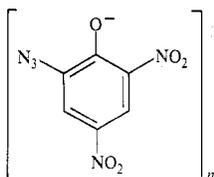
¹⁶ Butler, R. N., *Leicester Chem. Rev.*, 1969, 10, 12; Butler, R. N., *Adv. Heterocycl. Chem.*, 1977, 21, 323.

Compound (2) was also converted into the intermediate disodium 5,5'-azobis(tetrazolate) pentahydrate (8) by oxidative coupling with permanganate according to the method of Thiele.¹⁷ Reaction of (8) with thallos nitrate and basic lead nitrate gave the desired dithallos (9) and basic lead (10) salts respectively. 5,5'-Hydrazobis(1*H*-tetrazole) (11) was synthesized by reduction of (8) with magnesium in water.¹⁴

Reduction of picric acid to sodium picramate with sodium sulfide-sodium bicarbonate¹⁸ followed by diazotization gave 6-diazo-2,4-dinitrophenolate (12). 6-Diazo-2,4-dinitro-3-methylphenolate (13) was synthesized by the analogous reaction sequence from 3-methyl-2,4,6-trinitrophenol. Compound (12) was also used as a synthetic intermediate; reaction with sodium azide, as described by Glowiak,¹⁹ gave sodium 6-azido-2,4-dinitrophenolate (14) while reaction with potassium azide gave the potassium salt (15). The silver (16), lead (17) and barium (18) salts were obtained by reaction of solutions of (14) with the corresponding metal nitrates.

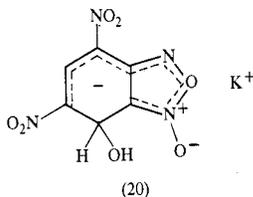


(12) R = H
(13) R = Me



(14) M = Na⁺
(15) M = K⁺
(16) M = Ag⁺
(17) M = Pb²⁺
(18) M = Ba²⁺

Hg(ONC)₂
(19)



(20)

Mercuric bisfulminate (19)^{6b} and 'potassium dinitrobenzofuroxan' (20)^{20*} were prepared as described in the literature.

Ignition temperatures for the 17 compounds were determined at a heating rate of 5°C/min and are listed in Table 1. The ignition temperature for (5) is significantly higher than reported¹⁴ and probably reflects greater purity of our product which was prepared from purified (3) whereas Jenkins and White used the unpurified copper salt.¹⁴ In contrast, the values for (14)–(18) are markedly lower than reported previously¹⁹ resulting from the different methods used; Glowiak dropped samples on to a heated plate and recorded the minimum temperature at which ignition occurred within 5 s.

* 'Potassium dinitrobenzofuroxan' is the name employed in the explosives literature for this compound. *Chemical Abstracts* lists it as 'K salt of 4,6-dinitrobenzofurazan 1-oxide'. Under IUPAC rules, the best name for structure (20) is potassium 4-hydroxy-5,7-dinitro-4,5-dihydrobenzofurazanide 3-oxide.

¹⁷ Thiele, J., *Justus Liebigs Ann. Chem.*, 1898, **303**, 57.

¹⁸ Hodgson, H. H., and Ward, E. R., *J. Chem. Soc.*, 1945, 663.

¹⁹ Glowiak, B., *Bull. Acad. Pol. Sci.*, 1960, **8**, 5; Glowiak, B., and Smolensky, D., *Chem. Stosow.*, 1960, **4**, 253 (*Chem. Abstr.*, 1960, **54**, 24475c).

²⁰ Norris, W. P., and Osmundsen, J., *J. Org. Chem.*, 1965, **30**, 2407.

Lead azide type RD1343²¹ was chosen as the substrate for determining sensitizing ability because it is readily available and is commonly used in initiating compositions. Experimental compositions were prepared by mixing each of the 17 sensitizers with lead azide RD1343 in the ratio 1 : 10. Experimental detonators were prepared by pressing an increment of lead monoxide (300 mg) followed by the experimental composition (55 mg) into mild steel tubes at 600 MPa. The lead monoxide functions as an inert back filling and ensures that the explosive pellet remains intact during penetration by the needle. Any initiation therefore results directly from the needle on the pellet and not by processes such as cracking of the pellet or friction between the needle or pellet on a hard backing surface. The experimental detonators differed from conventional stab detonators in that they were not fitted with a closing disc nor were they spotted with varnish.

Table 1. Ignition temperatures for pure sensitizer and stab initiation energies for 1 : 10 admixtures with lead azide RD1343

Sensitizing agent	Ignition temp. (°C)	Stab initiation energies (mJ)
Tetrazene (1)	136	3·3
Mercuric bis(5-nitrotetrazolate) (4)	206	34·3
Mercurous bis(5-nitrotetrazolate) (5)	205	185
Silver 5-nitrotetrazolate (6)	261	> 280
5-Nitro-2-picryltetrazole (7)	156	11·1
Dithalious 5,5'-azobis(tetrazolate) (9) ^A	212	18·3
Dilead 5,5'-azobis(tetrazolate) dihydroxide (10)	230	15·4
5,5'-Hydrazobis(1 <i>H</i> -tetrazole) (11)	229	> 280
6-Diazo-2,4-dinitrophenolate (12) ^A	160	5·2
6-Diazo-3-methyl-2,4-dinitrophenolate (13) ^A	178	9·4
Sodium 6-azido-2,4-dinitrophenolate (14) ^A	131	7·5
Potassium 6-azido-2,4-dinitrophenolate (15) ^A	133	6·5
Silver 6-azido-2,4-dinitrophenolate (16)	122	7·6
Lead bis(6-azido-2,4-dinitrophenolate) (17)	126	11·2
Barium bis(6-azido-2,4-dinitrophenolate) (18) ^A	159	23·0
Mercuric bisfulminate (19)	158	6·1
Potassium 4-hydroxy-5,7-dinitro-4,5-dihydro-benzofurazanide 3-oxide (20) ^A	200	15·4
Lead azide RD1343 ^B	316	c. 1000

^A Mixes poorly with lead azide RD1343.

^B For comparison.

Several of the sensitizers mixed poorly with the much denser lead azide and the compositions tended to separate. An ideal sensitizer should consist of crystals of suitable density and form to give good mixing with the other component(s) in the mixture. The sensitizers with poor mixing properties (Table 1) were either light fluffy needles or platelets; mixing could be improved by suitable crystal modification of the sensitizer. Such variation in crystal size and shape will affect stab sensitivity although the effect will be minimized since the crystals are crushed during pressing. We expect to examine the effect of modification of crystal habit on sensitizing ability in the near future.

²¹ Holloway, K. J., Taylor, G. W. C., and Thomas, A. T., Report No. 7/R/58 (1958), Explosives Research and Development Establishment, Waltham Abbey, Essex, U.K.

Stab initiation energies were determined by the use of a free falling needle of a similar design to strikers used in fuses. Preliminary determinations were conducted at a number of heights to obtain an approximate 50% fire level. The needle height was then varied by using regular intervals of 10% of this fire level. Each experiment was assessed as fire or no fire by sound (very loud!) and close visual inspection of the detonator tube. No partial ignitions which failed to propagate were detected even under microscopic examination. At least 25 detonators were tested for each composition. The results were analysed by using the Bruceton method²² and represent the 50% fire level. The stab initiation energies are listed in Table 1 and are shown plotted against sensitizer ignition temperatures in Fig. 1. Results for (5), (6) and (11) are not included in Fig. 1.

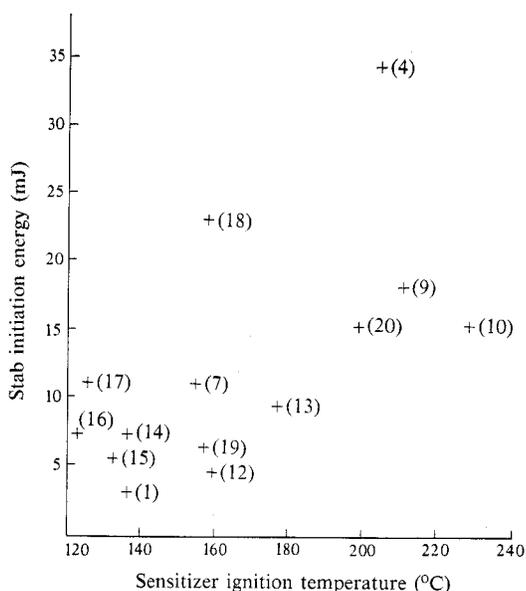


Fig. 1. A plot of stab initiation energies for binary (10 : 1) mixtures of lead azide RD1343 with a number of energetic sensitizers against the ignition temperature of the sensitizer. Note that the points for (5), (6), and (11), which would be well off scale, are not included.

Discussion

The results illustrated in Fig. 1 demonstrate a general trend towards increased sensitization, i.e. decreased stab initiation energies, as sensitizer ignition temperature decreases. This is a clear indication that ignition of the sensitizer is a key step in the stab initiation process. Statistical analysis of the data reveals a poor overall correlation, particularly if the results for (5), (6) and (11) (not included in Fig. 1, see Table 1) are included. The earlier correlation by Bird¹² for sensitization of service lead azide would appear to result from the limited number and fortuitous choice of sensitizers which were studied. Although service lead azide is slightly more sensitive to mechanical initiation than RD1343²¹ the difference is insufficient to markedly alter the results.*

* The stab initiation energy for service lead azide which was reported to be 50 mJ¹² is obviously in error and should be at least 500 mJ.

²² Culling, H. P., NAVORD Report 2101 (1953), U.S. Naval Ordnance Laboratory, Whiteoak, Md, U.S.A.

We can at this stage envisage initiation of the sensitized mixture as an initial degradation of the mechanical energy of the striker to heat and in particular to the formation of localized 'hot spots'. If the hot spot temperature exceeds the ignition temperature the sensitizer particles in the immediate vicinity ignite and in turn ignite the lead azide, which then detonates. Since the correlation between stab initiation energy and sensitizer ignition temperature is not exact, the sensitizer must be involved, in some cases, with generation of the hot spots. The stab initiation of L-mixture,* which is a sensitized mixture of lead dinitroresorcinate (50%), barium nitrate (45%) and tetrazene (5%), has been studied by high speed photography.¹¹ It was found that initiation occurred at a number of points both at and away from the needle. In contrast a homogeneous compact of (10) ignited only at or near the needle tip and a penetration of about 0.5 mm was usually necessary before initiation occurred. Hot spot formation can occur by two frictional processes: friction between the needle and hard explosive or grit particles, or between neighbouring hard particles. Evidence from the photographic study¹¹ demonstrates that both these mechanisms are important for stab initiation of sensitized mixtures.

This result can be contrasted with those for homogeneous (non-sensitized) compacts. Chaudhri¹³ calculated the temperature rise produced by penetration of a needle into an explosive compact using a model whereby hot spots arose by friction between the needle surface, explosive particles attached to the needle and the bulk explosive. The temperature rise produced by impact of a 145 g striker on a lead azide compact was calculated to be 118°. The calculated temperature rise for a compact of (10), which has similar physical properties to lead azide but a higher coefficient of friction,† was 237°, i.e. higher than the ignition temperature. Although these calculations do not apply directly to our results since different striker and detonator geometries were used, the trends should still follow. Indeed, lead azide has low sensitivity to stab initiation (initiation energy *c.* 1000 mJ) while (10), with its higher friction coefficient leading to higher hot spot temperatures coupled with its lower ignition temperature, can be readily initiated (initiation energy 7.6 mJ).‡ Chaudhri's calculations, combined with the photographic evidence,¹¹ strongly suggest that friction between needle and explosive is by far the most important mechanism for initiation of homogeneous compacts.

A feature of the results in Table 1 is that sensitizers with ignition temperatures below 180°, with the single exception of (18), afford excellent sensitization while the behaviour of those with ignition temperatures above 180° is much less predictable. The prediction from Chaudhri's calculations would be that friction between the needle and lead azide should generate hot spot temperature rises sufficient to ignite sensitizers with ignition temperatures below 180°. Temperatures above 200° would not be expected at the low striker energies used here. However, if the sensitizers are hard and gritty, hot spots could also be generated by friction between the needle and

* The term L-mixture is a British composition also referred to as RD 1651.

† Lead azide has a coefficient of friction of 0.28, determined either on single crystals or thin films.²³ The corresponding value for (10) does not appear to have been reported—Chaudhri states it to be 'twice that for lead azide'.¹³ Coefficients of friction have not been determined for most of the compounds (1)–(20).

‡ Determined on experimental detonators of (10) (55 mg) with lead monoxide (300 mg) backfilling prepared exactly as described for the sensitized mixtures.

²³ Amuzu, J. K. A., Briscoe, B. J., and Chaudhri, M. M., *J. Phys. D*, 1976, 9, 133.

sensitizer particles or lead azide and sensitizer particles. Such a process would be doubly advantageous in that higher temperatures could be generated and they would be generated 'in situ' with the sensitizer. This would be an explanation for the variation in behaviour of the structurally related salts (9) and (10), and their organic counterpart (11). Compounds (9) and (10), which are hard gritty materials in comparison with (11), afford reasonable sensitization while (11) does not sensitize despite the similarity of the ignition temperatures.

Table 2. The effect of variation of sensitizer content on stab initiation energies for admixtures of lead azide RD1343 with tetrazene (1) and 5-nitro-2-picryltetrazole (7)

Sensitizer content (%) ^A	Stab initiation energies (mJ)		Sensitizer content (%) ^A	Stab initiation energies (mJ)	
	(1)	(7)		(1)	(7)
100	> 280	106.1	4.8	3.5	9.4
50	7.9		2.0	3.6	8.6
23.1	4.7		1.0	6.1	13.6
16.7		23.4	0.0	c. 1000	c. 1000
9.1	3.3	11.1			

^A Content is percentage of total mass (sensitizer + lead azide).

Further evidence for the importance of frictional processes, as opposed to mechanisms such as adiabatic compression of interstitial gases,^{1,2,9} can be seen from the stab initiation energies for a series of compositions of lead azide RD1343 containing varying percentages of (1) and (7) (Table 2). Optimum sensitization is exhibited by mixtures containing 2–9.1% of sensitizer. Further increase in sensitizer content leads to decreased sensitization, a result consistent with (1) and (7) being relatively soft materials which 'dilute' and hence desensitize the hard lead azide. As homogeneous compacts, (1) showed no sensitiveness to stab initiation* over the range of energies investigated and (7) exhibited only moderate sensitivity (Table 2), despite their low ignition temperatures. This again emphasizes the importance of friction between the needle and hard particles, or adjacent hard particles, to initiate reaction. No experimental studies directed towards quantifying the role of hardness in stab initiation have as yet been published. The decrease in sensitization at 1% sensitizer concentration presumably results from the lower probability of finding a sensitizer particle in the vicinity of the hot spot.

Conclusion

The results obtained in this study support the concept that stab initiation occurs principally by conversion of mechanical energy into heat through friction. We have identified some of the ways that energetic materials can sensitize a hard primary explosive to stab initiation. Clearly, optimum sensitization would be achieved by a hard crystalline solid with a low ignition temperature and high friction coefficient. Our future studies of new energetic sensitizers will concentrate on materials with

* The stab initiation energy of (1) has been reported previously as 35 mJ.¹² We have reinvestigated (1) and have not obtained any ignitions or partial ignitions up to energies of 280 mJ. Samples were inspected microscopically before and after needle penetration and no ignition of material contacted directly by the needle had occurred. At 280 mJ the needle penetrated through to the lead oxide backing, hence higher energies were not used.

ignition temperatures below 180°C. Although our results support the hypothesis that the sensitizing ability of tetrazene results primarily from its low ignition temperature,¹² they also emphasize the 'unique' properties of this material, e.g. it has low sensitivity to stab initiation as a homogeneous compact but provides the maximum sensitization to lead azide of all the materials studied here despite the fact that some have lower ignition temperatures. A number of other material properties in addition to those referred to already which may be potentially important include diffusivity and heat capacity as well as activation energies and enthalpies of thermal decomposition. The role of such variables must be defined before a full understanding of the stab initiation process can be obtained.

Experimental

CAUTION! The explosive materials described in this report are extremely sensitive to mechanical and electrostatic stimulæ. Preparations should be carried out by using remote handling apparatus for large-scale reactions (> 2 g) and behind suitable protective screening for small-scale (< 2 g) preparations. Laboratories and personnel should be properly earthed. All products should be filtered by means of gravity filtration unless specified, manipulated only with wooden or paper (not metal) spatulas and stored in conducting containers.

All chemicals except those which were synthesized as described below were available commercially or from previous studies. Ignition temperatures were determined on an instrument built to specifications for the ERDE* temperature of ignition test. Samples of 50 mg were heated at 5°/min and measurements were performed in triplicate. Infrared spectra were recorded on a Unicam SP 1000 spectrophotometer and ¹H n.m.r. spectra were recorded at 60 MHz on a Varian HA 60 IL spectrometer with tetramethylsilane as internal reference. Microanalyses were performed by AMDEL and the Australian Microanalytical Service, Melbourne.

Thermal behaviour was studied optically at a heating rate of 10°/min by using a Leitz Ortholux microscope with an attached Mettler FP-2 hot stage. None of the explosive samples exhibited a distinct melting point. Heating initially produced outgassing and/or crystal break-up which accelerated with increased temperature. Liquid products were subsequently formed in some cases. Authenticity and purity of products were confirmed by comparison with reported ignition temperatures (where available) and crystal colours and form. Variation between ignition temperatures observed here and reported previously is discussed in the Results section.

No attempt has been made to optimize experimental yields, which were typically at least 50%.

Lead Azide RD1343

Lead azide RD1343 was obtained as a single batch from M.F.F., St. Marys, N.S.W.; ignition temp. 315°, 316(2 ×)° (lit.²¹ 320°).

1-(1H-Tetrazol-5-yl)tetraz-1-ene-3-carboximidamide Monohydrate ('Tetrazene') (1)

The material used was type RD1357 and was available as a single batch from a sample prepared at Materials Research Laboratories for other studies. Ignition temp. 136(2 ×)°, 137°.

Sodium 5-Nitrotetrazolate Dihydrate (3)¹⁵

Sodium 5-nitrotetrazolate dihydrate (3) was prepared from tetrazol-5-amine hydrate (2) according to the method of Gilligan and Kamlet.¹⁵ The product was purified by dissolution in the minimum of boiling acetone followed by filtration and precipitation by addition of an equal volume of hexane. The solution was allowed to cool and the product filtered under suction. Compound (3) was obtained as irregular, chunky white crystals; ignition temp. 202°, 210°, 214° (lit.¹⁴ 202°).

* Explosives Research and Development Establishment, Waltham Abbey, Essex, U.K. Since 1977 it has undergone a name change and is now PERME (Propellants, Explosives and Rocket Motor Establishment).

*Mercuric Bis(5-nitrotetrazolate) (4)*¹⁴

A solution of (3) (11.6 g) in water (195 ml) and conc. nitric acid (22 ml) was heated to 80°. A solution of mercuric nitrate dihydrate (18 g) in water (100 ml) and conc. nitric acid (2 ml) was added with stirring over 50 min, then the reaction allowed to cool to 20°. Compound (4) was obtained by filtration as agglomerations of tiny white crystals; ignition temp. 205(2×)°, 207° (lit.¹⁴ 205°, 208°).

Mercurous Bis(5-nitrotetrazolate) (5)

A solution of mercurous nitrate dihydrate (4.6 g) in water (20 ml) and conc. nitric acid (0.5 ml) was added dropwise, with stirring, to a solution of (3) (4.12 g) in water (200 ml) and conc. nitric acid (1 ml) at 90° over 20 min. After complete addition, the mixture was cooled to 50°, filtered and the product washed with water and acetone. Compound (5) was obtained as short white rhombohedra; ignition temp. 204°, 206(2×)° (lit.¹⁴ 160°, 165°).

Silver 5-Nitrotetrazolate (6)

A solution of silver nitrate (2.35 g) in water (55 ml) was added over 30 min to a stirred solution of (3) (1.7 g) in water (50 ml). After complete addition, 1 M nitric acid (10 ml) was added in one lot and the reaction stirred for a further 10 min. The reaction was allowed to cool and filtered to give (6) as small irregular white crystals; ignition temp. 261(3×)° (lit.¹⁴ 262°, 265°).

5-Nitro-2-picryltetrazole (7)

Sodium 5-nitrotetrazolate anhydrate,* prepared by dehydrating (3) (3.5 g) at 70° and 133 Pa for 24 h, was added to dry acetone (30 ml). Picryl chloride (5.0 g) was added in one portion, the flask stoppered, swirled for a minute, then allowed to stand for 48 h. The reaction was filtered under suction, the solid product (sodium chloride) washed with a small volume of acetone and the filtrate concentrated to 25 ml. Hexane (27 ml) was added to the hot solution. Crystallization commenced upon cooling and was completed after standing overnight. Suction filtration gave 5-nitro-2-picryltetrazole (7) as clumps of very small, slightly yellow crystals which could cautiously be broken up with a wooden spatula; ignition temp. 155°, 156°, 158° (explodes violently) (Found: C, 25.8; H, 0.7; N, 34.0. C₇H₂N₈O₈ requires C, 25.8; H, 0.6; N, 34.3%). ν_{\max} (KBr): 3030, 1600, 1550, 1530, 1348, 1320, 1313, 1290, 1073, 979, 971, 895, 814 cm⁻¹. ¹H n.m.r. (CDCl₃): δ 9.58, s. A second crop could be obtained by repeating the recrystallization procedure.

*Disodium 5,5'-Azobis(tetrazolate) Pentahydrate (8)*¹⁷

A solution of tetrazol-5-amine hydrate (10.0 g) in 15% aqueous sodium hydroxide (100 ml) at 100° was treated portionwise with powdered potassium permanganate. After about 12.5 g had been added, further addition gave no discernible reaction and the still hot solution was treated dropwise with ethanol and hot filtered. Compound (8) crystallized upon cooling and was purified by recrystallization from water to give compact yellow crystals.

Dithalious 5,5'-Azobis(tetrazolate) (9)

A solution of thalious nitrate (2.65 g) in water (20 ml) was added dropwise, with stirring, to a solution of (8) (1.5 g) in water (25 ml) at 70° over 10 min. Stirring was continued for 5 min and, upon cooling, (9) deposited as small yellow needles which were isolated by filtration. Ignition temp. 212°.

Dilead 5,5'-Azobis(tetrazolate) Dihydroxide (10)

A solution of lead acetate trihydrate (12.6 g) in water (50 ml) was added dropwise, with stirring, to a solution of (8) (6.2 g) in water (100 ml) and conc. ammonia (3.8 ml) at 90° over 40 min. Stirring was continued for 5 min and then the solution cooled to 50° and filtered. Compound (10) was obtained as bright yellow rhombohedra. Ignition temp. 230(2×)°, 231(2×)°.

* CAUTION: Sodium 5-nitrotetrazolate anhydrate is extremely sensitive to mechanical initiation. It should be treated as a primary explosive.

5,5'-Hydrazobis(1H-tetrazole) (11)¹⁴

A suspension of (8) (7.0 g) and magnesium turnings (3.5 g) in water (300 ml) was heated at reflux for 24 h. The solution changed from bright yellow to colourless and a colourless suspension formed. The reaction was cooled to 80°, filtered under suction then quickly acidified with 25% aqueous nitric acid (8 ml). Upon cooling, (11) deposited as small colourless prisms which were isolated by filtration under suction. Ignition temp. 228°, 229°, 230° (lit.¹⁴ 206°, 208°).

6-Diazo-2,4-dinitrophenolate (12)²⁴

A solution of sodium nitrite (3.7 g) in water (50 ml) was added in one portion to a rapidly stirred solution of sodium picramate (12.0 g, prepared by reduction of picric acid according to the method of Hodgson and Ward¹⁸) in 5.5% hydrochloric acid (150 ml). The solution was stirred for 1 h then the product filtered and washed with water. Recrystallization from acetone/water gave (12) as bronze platelets; ignition temp. 160(2×)°, 161°.

6-Diazo-3-methyl-2,4-dinitrophenolate (13)

Conc. ammonia solution was added dropwise to a stirred solution of 3-methyl-2,4,6-trinitrophenol (14.6 g) in methanol (140 ml) at 60° until the solution was just neutral (litmus). A solution of sodium sulfide nonahydrate (40 g) and sodium bicarbonate (14 g) in water (66 ml) was then added dropwise over 1 h and the resulting mixture stirred at 60° for 24 h. The reaction was refrigerated overnight, chilled water (210 ml) was added, followed by filtration under suction, to give sodium 3-methylpicramate as a reddish brown powder (12.2 g) which was used without further purification.

A solution of sodium nitrite (0.66 g) in water (10 ml) was added in one portion to a rapidly stirred solution of sodium 3-methylpicramate (2.25 g) in 5.5% hydrochloric acid (30 ml) at 15°. The reaction was stirred for 1 h, filtered, the product washed with water and recrystallized from acetone/water to give the *phenolate* (13) as grey-bronze platelets, ignition temp. 177°, 178°, 179° (Found: C, 37.7; H, 1.9; N, 24.7. C₇H₄N₄O₅ requires C, 37.5; H, 1.8; N, 25.0%). ν_{\max} (KBr): 3080, 2177, 1627, 1612, 1568, 1535, 1525, 1332, 1309, 750, 715, 707, 675 cm⁻¹. ¹H n.m.r. (CD₃COCD₃): δ 2.45, s, 3H, CH₃; 9.02, s, 1H, H 5.

Sodium 6-Azido-2,4-dinitrophenolate (14)

A solution of sodium azide (0.33 g) in water (3.25 ml) was added dropwise with stirring to a solution of (12) (1.05 g) in acetone (25 ml) at 40°. Vigorous evolution of nitrogen was observed during addition and stirring was continued for 30 min. This solution was used for preparation of the silver, lead and barium salts described below.

Compound (14) was isolated by allowing the solution to evaporate almost to dryness and then drying the product between filter paper. The product was obtained as clumps of tiny orange needles; ignition temp. 131(2×)°, 132° (lit.¹⁹ 218°).

Potassium 6-Azido-2,4-dinitrophenolate (15)

A solution of potassium azide (0.41 g) in water (4.1 ml) was added dropwise with stirring to a solution of (12) (1.05 g) in acetone (25 ml) at 40°. The solution turned dark red with evolution of nitrogen and a red-brown precipitate formed. Stirring was discontinued and the reaction was held at 40° for 1 h, then cooled to room temperature. Compound (15) was isolated by filtration as tiny red-brown needles which tended to agglomerate. Ignition temp. 132°, 133°, 135°.

Silver 6-Azido-2,4-dinitrophenolate (16)

A solution of (14), prepared as above, was cooled to 25° and treated dropwise with a solution of silver nitrate (1.0 g) in water (10 ml). A yellow precipitate formed immediately and after complete addition the reaction was allowed to stand at room temperature for 2 h, then filtered and washed with aqueous acetone. The product formed a solid cake upon drying and was cautiously broken up with a wooden spatula. Compound (16) was obtained as clusters of tiny yellow crystals; ignition temp. 122(2×)°, 123° (lit.¹⁹ 178°).

²⁴ Clark, L. V., *Ind. Eng. Chem.*, 1933, **25**, 663.

Lead Bis(6-azido-2,4-dinitrophenolate) (17)

A solution of (14), prepared as above, was cooled to 25° and treated dropwise with a solution of lead nitrate (1.0 g) in water (10 ml). Towards the end of the addition, crystals began to separate and the flask was left for 4 h to complete crystallization. Compound (17) was isolated by filtration as fluffy brownish needles; ignition temp. 125°, 126(2×)° (lit.¹⁹ 168°).

Barium Bis(6-azido-2,4-dinitrophenolate) (18)

A solution of (14), prepared as above, was cooled to 25° and treated dropwise with a solution of barium nitrate (0.78 g) in water (10 ml). Crystallization commenced after about 2 h and was completed by standing overnight. Compound (18) was isolated by filtration as fluffy bronze needles; ignition temp. 158°, 159°, 161° (lit.¹⁹ 197°).

Mercuric Bisfulminate (19)

Mercury (7.6 g) was dissolved in conc. nitric acid (65 ml), the solution made up to 80 ml with water, heated to 55° and then ethanol (65 ml) added in one portion. After the vigorous reaction had subsided the solution was filtered and the crystals washed with water then acetone and dried to give (19) as pale brown octahedra; ignition temp. 157(2×)°, 159° (lit.^{6b} 160–165°).

Potassium 4-Hydroxy-5,7-dinitro-4,5-dihydrobenzofurazanide 3-Oxide (20)

Sodium bicarbonate (2.1 g) was added to a solution of 4,6-dinitrobenzofurazan 1-oxide (5.4 g) in water (150 ml) at 70°. After effervescence had ceased, the solution was filtered while still hot then a solution of potassium nitrate (2.8 g) in water (100 ml) was added over 5 min at 70°. Upon cooling, the *potassium salt* (20) deposited as small golden orange plates which were recovered by filtration. Ignition temp. 199°, 200°, 201° (lit.²⁰ explodes at 210°).

Preparation of Sensitized Mixtures

The energetic sensitizers were initially sieved remotely through a 300-micron sieve to break up aggregates and ensure reasonable homogeneity of particle sizes. Explosive compositions were prepared by adding the sensitizer (0.20 g) to lead azide RD1343 (2.00 g). Mixing was achieved by cautiously placing the mixture on to a sheet of paper and fold mixing. A number of the sensitized mixes tended to separate upon standing (see Table 1 and text). These compositions were remixed immediately prior to preparation of the experimental detonators.

Preparation of Experimental Detonators

Experimental detonators were prepared in mild steel tubes, 6 mm o.d., 3.2 mm i.d., length 6 mm by using a Pongrass press at a pressure of 600 MPa. An initial increment of lead monoxide (300 mg) was added and pressed then the experimental composition (55 mg) was added on top and the unit repressed. Under these conditions the top of the explosive compact was visually flat and almost flush with the top of the detonator tube.

Determination of Stab Initiation Energies

The experimental set up, consisting of a drop tower test rig fitted with a quick release mechanism, has previously been described in detail.²⁵ A 14.5 g striker was normally used although a 55.2 g striker was used for the less sensitive compositions of (5), (6) and (11) with lead azide RD1343. The result for pure lead azide RD1343 was obtained by using a 135 g striker. The striker body was refitted with a new needle after every test whether or not a fire occurred. The needle was silver steel hardened to 650 HV with a 0.08–0.20 mm flat on the tip. In each experiment the striker was released from a pre-set height to impact on the experimental detonator supported in an aluminium holder held in a mild steel base. Each testing was assessed as 'fire' or 'no fire' by sound (very loud for a positive 'fire') and visual inspection of the detonator tubes. A 'fire' resulted in splaying and cracking

²⁵ Bentley, J. R., and Elischer, P. P., Report No. MRL-R-776 (1980), Materials Research Laboratories, Maribyrnong, Vic.

of the tube and ejection of much of the lead monoxide. A 'no fire' resulted only in an obvious indentation into the compacted explosive. The detonators were not retested after a 'no fire' and were destroyed chemically.

A minimum of 25 detonators were tested for each experimental composition. Results were analysed by the Bruceton method²² and represent the 50% fire level. Standard deviations have not been included; the Bruceton method of analysis is designed to give an overall estimate of the population from a limited number of samples. Statistical interpretation of the results derived from sample sizes used here give a reliable estimate of 50% functioning levels but not for standard deviations.

Acknowledgments

Mr L. D. Redman, Mr G. Cleal, Mr A. M. Pitt, Mrs M. J. Myers and Mr E. Vella are thanked for technical assistance.

Manuscript received 9 June 1981