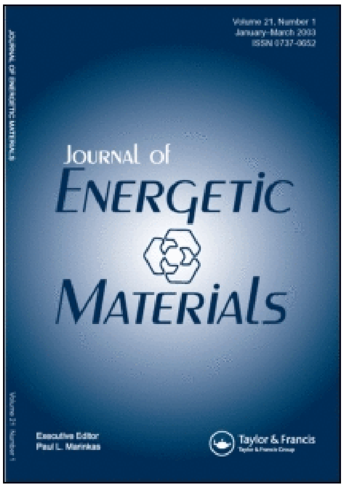

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Contamination of Explosive Materials with N-Methylpyrrolidin-2-One (NMP)

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Several explosive materials, viz., triaminotrinitrobenzene, (TATB), hexanitrostilbene, (HNS), and 1,1-diamino-2,2-dinitroethene (FOX-7), that had been processed using the solvent N-methylpyrrolidin-2-one (NMP) were found by ^{1}H *NMR and head-space GC-MS to be contaminated with small amounts (0.15–0.2 wt% for TATB 0.1–0.5 wt% for HNS and 0.1–0.2 wt% for FOX-7) of this solvent. Attempts to reduce the level of contamination by a variety of methods were only partially successful.*

Introduction

Solvents are widely used in the production of energetic materials, and N-methylpyrrolidin-2-one (NMP), in recent years, has found increased use in this area on account of its good solvent properties, its miscibility with water, and its biodegradability. Some explosive materials have been precipitated from NMP, either during their formation for example, TATB (triaminotrinitrobenzene) [1], or during their conversion to finely divided, high surface area forms, for example HNS IV (high surface area hexanitrostilbene) [2]. Some have also been digested or recrystallized from NMP in order to effect

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purification, for example, TATB, HNS II (high bulk density hexanitrostilbene) [3], and FOX-7 (1,1-diamino-2,2-dinitroethene) [4]. During a head-space GC-MS study of some TATB [1] samples whose synthesis had involved contact with NMP at some stage, we discovered that NMP vapor was released into the head-space even on storage at room temperature. This indicated that the samples contained some NMP even though other analytical data (DSC, vacuum stability tests) [1, 5] had indicated that the samples were of excellent quality. We report here the results of an investigation into the level of contamination by NMP in TATB samples, and in the other explosive materials that had been processed using NMP, viz., HNS (recrystallized and types II and IV) and FOX-7, and the results of various attempts to remove this contaminant.

Experimental

Origin of NMP-contaminated Samples

TATB sample 1. Synthesized from 1,3,5-tripropoxy-2,4,6-trinitrobenzene (TPTNB) as follows. TPTNB (15.0 g) dissolved in NMP (50 ml) was sealed in an autoclave, and NH_3 gas was introduced at 7–8 bar. This caused the temperature to rise to 40°C. The mixture was stirred at 20–40°C for 4 hr, and then heated at 107–110°C during 4 hr. The product was filtered off after cooling, washed with NMP (30 ml) and acetone (50 ml), and then dried. Yield: 9.9 g, particle size (Malvern) VMD: 19.5 µm.

TATB sample 2. TATB sample 1 (1.5 g) was dispersed in 5 vol% methanol/water (50 ml) in a beaker and treated with stirring during 2 hr in an ultrasonic bath (Camlab Transsonic model TS540, 35 kHz.) The solid was filtered off, washed thoroughly with distilled water, and dried. Particle size (Malvern) VMD: 14.0 µm.

TATB sample 3. TATB sample 1 extensively aged (see steps 1–8 under "Aging and head-space GC-MS analysis for NMP" below).

TATB sample 4. Synthesized from TPTNB as follows. TPTNB (5.5 g) was dissolved in diethyl ether (40 ml) and added to liquid NH_3 (20 ml) and then refluxed during 2 hr. The NH_3 was allowed to evaporate, and the solid (96%) was filtered off. A portion of the solid (1.0 g) was digested in NMP (10 ml) at 100°C during 4 hr; the product was filtered off, then washed with acetone and dried. Particle size (Malvern) VMD: 103 µm.

HNS sample 1. HNS II was recrystallized as follows. HNS II (12 g) was dissolved in NMP (80 ml) at 125°C and cooled rapidly in ice water to give fine needles of HNS. The solid was filtered off, washed with MeOH (2 × 15 ml with suction, 2 × 25 ml with stirring, 1 × 15 ml with suction), and dried. Particle size (Malvern) VMD: 155 µm.

HNS sample 2. HNS II was recrystallized as follows. HNS II (12 g) was dissolved in NMP (80 ml) at 125°C and cooled without stirring in the oil bath to give coarse needles of HNS. The solid was filtered off, washed with MeOH (2 × 15 ml with suction, 2 × 25 ml with stirring, 1 × 15 ml with suction), and dried. Particle size (Malvern) VMD: 388 µm.

HNS sample 3. HNS sample 2 (5.5 g) was dispersed in 5 vol% methanol/water (100 ml) in a beaker and treated with stirring during 2 hr in an ultrasonic bath. The solid was filtered off, washed thoroughly with distilled water, and dried. Particle size (Malvern) VMD: 54 µm.

HNS sample 4. HNS sample 1 extensively aged (see steps 1–8 under "Aging and head-space GC-MS analysis for NMP" below).

HNS sample 5. HNS sample 2 extensively aged (see steps 1–8 under "Aging and head-space GC-MS analysis for NMP" below).

HNS sample 6. HNS sample 1 (100 mg) was washed with dioxan-MeOH (1–4 by volume, 3 × 2 ml with stirring, 2 × 2 ml with suction), and then MeOH (3 × 2 ml with stirring, 2 × 2 ml with suction).

HNS sample 7. HNS sample 2 (100 mg) was washed with dioxan-MeOH (1–4 by volume, 3 × 2 ml with stirring, 2 × 2 ml with suction), and then MeOH (3 × 2 ml with stirring, 2 × 2 ml with suction).

HNS IV sample 1. HNS II (3.57 g) was dissolved in NMP (150 ml) at 100°C and then crash precipitated by addition to water (675 ml) at 80°C. The solid was filtered off and washed thoroughly with water. Specific area 12 m^2/g. Particle size (Malvern) VMD: ~4 µm.

HNS IV sample 2. HNS IV sample 1 (100 mg) was washed with dioxan-MeOH (1–4 by volume, 3 × 2 ml with stirring, 2 × 2 ml with suction), and then MeOH (3 × 2 ml with stirring, 2 × 2 ml with suction).

FOX-7 sample 1. FOX-7 was recrystallized as follows. FOX-7 (3.0 g) was dissolved at 100°C in 50 vol% NMP/H_2O (48 g), and then cooled with stirring to room temperature. The solid was filtered off, washed thoroughly with methanol, and dried. Yield: 2.11 g, particle size (Malvern) VMD: 159 µm.

FOX-7 sample 2. FOX-7 sample 1 (2.5 g) was dispersed in 5 vol% methanol/water (55 ml) in a beaker and treated with stirring during 2 hr in an ultrasonic bath. The solid was filtered off, washed thoroughly with distilled water, and dried. Particle size (Malvern) VMD: 123 µm.

FOX-7 sample 3. FOX-7 sample 1 extensively aged (see steps 1–8 under "Aging and head-space GC-MS analysis for NMP" below).

Graphite sample 1. Graphite was treated with NMP as follows. A suspension of graphite (10.0 g) in NMP (50 ml) was heated at 100°C during 23 hr. The solid was filtered off, washed with MeOH (2 × 15 ml with suction, 2 × 25 ml with stirring, 1 × 15 ml with suction), and dried. Particle size (Malvern) VMD: 8.7 µm.

Measurement of NMP Content by ^1H NMR

For those samples that could be completely dissolved, the sample (~10 mg for HNS, 74 mg, 0.5 mmol for FOX-7) was dissolved in DMSO-d_6 (1.0 ml) and the ^1H spectrum recorded (Bruker DPX 250; 8000 pulses for HNS, 128 pulses for FOX-7). The ^1H NMR spectrum of NMP is shown in Figure 1, and a typical ^1H NMR spectrum of NMP-contaminated FOX-7 is shown in Figure 2. The NMP content (as mol%) was calculated from the integrals of the C-4 quintet of NMP at 1.9 ppm (2H; other NMP peaks were partially obscured) and the alkene protons of HNS (2H) or the NH protons of FOX-7 (4H).

For DMSO-insoluble samples (TATB, graphite), a sample (20 mg) was digested with stirring in DMSO-d_6 (1.0 ml) containing the reference compound 1,2-dichlorobenzene (5 µl of a standard solution 0.0777 mmol/ml) at 100°C during 20 hr. The insoluble material was

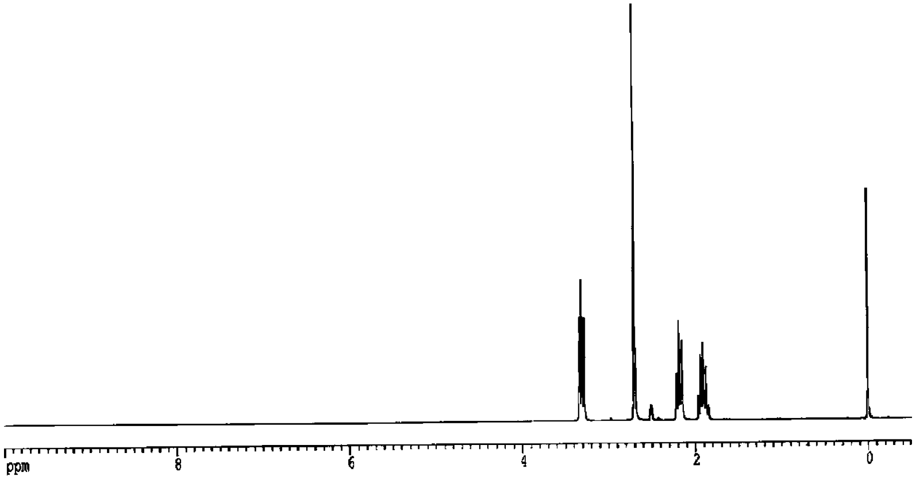

Figure 1. ^{1}H NMR spectrum of NMP in DMSO-d_6.

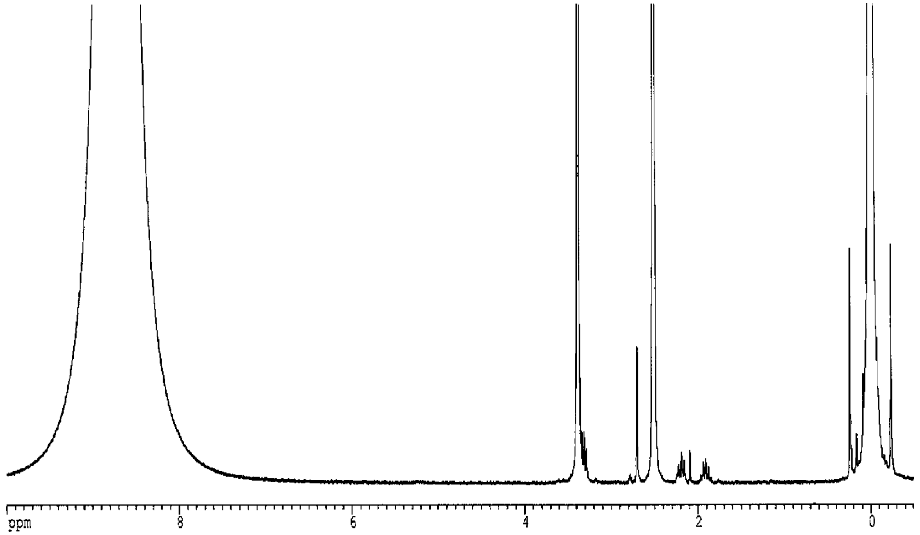

Figure 2. ^{1}H NMR spectrum of NMP-contaminated FOX-7 in DMSO-d$_6$.

then allowed to settle, and the extract was removed for NMR analysis (8000 pulses). The NMP content (as mmol in 20 mg sample) was calculated from the integrals of the C-4 quintet of NMP (2H) and the multiplet for 1,2-dichlorobenzene (2H) at 7.64 ppm. The results obtained represent minimum values since it was assumed that all NMP was extracted.

Aging and Head-Space GC-MS Analysis for NMP

One-half gram samples of each NMP-contaminated sample were sealed (in air) in 12 ml vials fitted with a PTFE-lined, self-sealing septum. The head-space gases were sampled after each aging stage.

1. Freshly washed with methanol (2 × 15 ml with suction, 2 × 25 ml with stirring, 1 × 15 ml with suction) and dried
2. Aged 7 days at room temperature
3. Aged 2 hr at 100°C
4. Removed from vial, rewashed with methanol (as 1) and resealed in a fresh vial
5. Aged 12 days at room temperature
6. Aged 7 days at room temperature
7. Aged 7 days at room temperature
8. Aged 8 days at room temperature and 2 hr at 100°C

GC-MS analyses were performed using a Thermo-Finnigan MD800 instrument using Xcalibur software. A CP-Sil 5 CB low-bleed column (length 15 m, ID 0.25 mm) was used, with He carrier gas (86 ml/min; 1:86 split at the detector). The gas sample (50 μl) was held at 50°C prior to injection onto the column at 50°C. After 2 min at 50°C, the temperature was raised at 10°C/min to 200°C, and then held at this temperature for 15 min. The results were presented both as a composite chromatogram of all components (total ion current), and as chromatograms of species with specified m/z ratios (see Figure 3). The integral values for NMP (RT 4.95 min, m/z 98.5–99.5) was calculated as the ratio to the integral for argon (Ar, RT 0.84 min, m/z 39.5–40.5), present as 0.93 vol% in air. This was then corrected for the response ratio (NMP 33.5 × more sensitive than Ar), and the number of moles of NMP in the head-space was calculated using the volume of air in the vial, and thus the volume and moles of Ar.

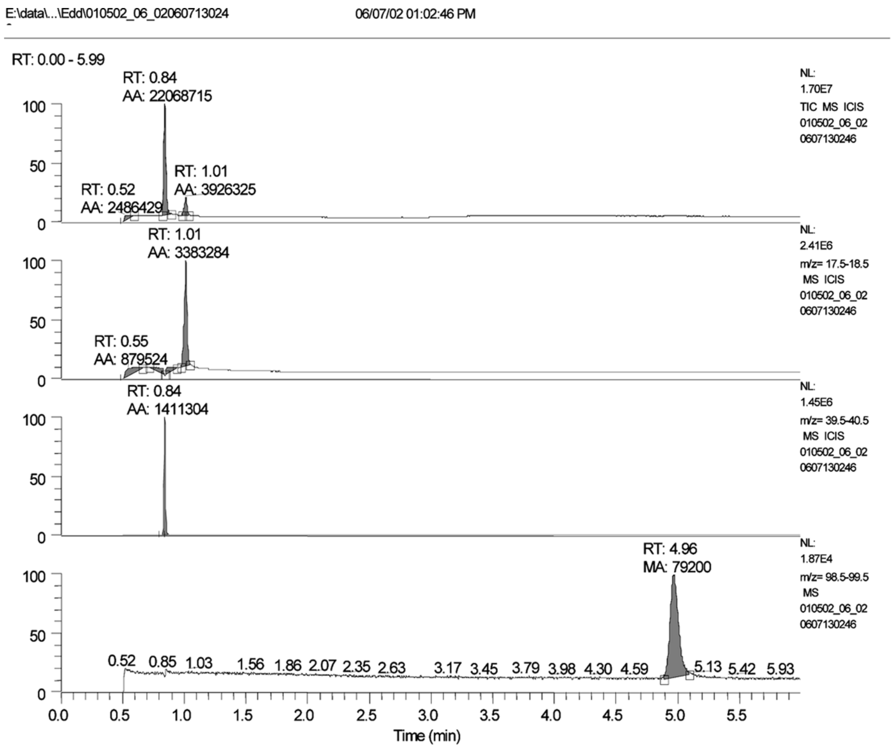

Figure 3. GC-MS head-space analysis for NMP.

Results and Discussion

The processing details of all of the materials studied are given in the Experimental section. Starting samples of TATB were produced [1, 5] from 1,3,5-tripropoxy-2,4,6-trinitrobenzene either by amination in NMP followed by digestion in NMP (TATB sample 1) or by amination in liquid ammonia followed by digestion in NMP (TATB sample 4). Starting samples of HNS were produced by either recrystallization from NMP [3] (HNS samples 1 and 2) or by crash precipitation from NMP [2] (HNS IV sample 1). The starting sample of FOX-7 was produced by recrystallization from water-NMP (FOX-7 sample 1).

Head-space GC-MS analysis, while giving an indication of the presence of NMP in a solid sample, cannot be used to obtain the actual level of contamination because the distribution of NMP between the solid and the gaseous phase is unpredictable (this is clearly demonstrated below). For the measurement of the degree of contamination ^{1}H NMR spectroscopy can be used. Ideally, the sample should be completely soluble in the NMR solvent. Both HNS and FOX-7 can be dissolved in DMSO-d_6, but for TATB, which is almost insoluble in this solvent, the NMP has to be extracted into the solvent for analysis. The concentration of NMP can be determined by integration of the proton absorption of any of the groups of peaks exhibited by NMP (in practice, only the quintet of the C-4 methylene group is free of other absorptions in the systems) relative to a suitable absorption exhibited by the substrate being analyzed, for example, alkene protons for HNS or NH protons for FOX-7, or relative to an added reference compound, for example, 1,2-dichlorobenzene for TATB extracts. The results of these analyses are given in Table 1.

The concentration of NMP in the various starting materials was 0.15–0.2 wt% for TATB, irrespective of whether the TATB was initially precipitated from NMP or simply digested in NMP, around 0.2 wt% for recrystallized HNS, 0.10 wt% for HNS II, around 0.5 wt% for HNS IV, and 0.1–0.2 wt% for FOX-7. Graphite, which has a layered crystal structure [6] similar to that of TATB [7] and FOX-7 [8], and which had been deliberately contaminated with NMP for comparison with these explosives, contained 0.1 wt%.

Since NMP had first been detected by head-space GC-MS analysis of a TATB sample, this technique was used to investigate the release of NMP from samples of TATB, HNS (fine and coarse), and FOX-7, all of which were known (from NMR analysis) to be contaminated with NMP. The amount of NMP released into the head-space

Table 1
NMP content as measured by ^{1}H NMR

Material	NMP content	
	mole %	% by weight
TATB sample 1	$(3.26 \times 10^{-4}$ mmol$)^1$	0.16
TATB sample 2 (sonicated)	$(2.92 \times 10^{-4}$ mmol$)^1$	0.14
TATB sample 3 (aged)	$(2.94 \times 10^{-4}$ mmol$)^1$	0.15
TATB sample 4 (NMP treated)	$(3.85 \times 10^{-4}$ mmol$)^1$	0.19
HNS sample 1 (fine)	0.87	0.19
HNS sample 2 (coarse)	0.93	0.21
HNS sample 3 (coarse sonicated)	0.50	0.11
HNS sample 4 (fine aged)	0.44	0.10
HNS sample 5 (coarse aged)	0.37	0.081
HNS sample 6 (fine washed)^2	0.15	0.033
HNS sample 7 (coarse washed)^2	0.38	0.084
HNS II	0.47	0.10
HNS IV sample 1	2.33	0.52
HNS IV sample 2 (washed)^2	0.00	0.00
FOX-7 sample 1a^3	0.25	0.17
FOX-7 sample 1b^3	0.17	0.11
FOX-7 sample 2 (sonicated)	0.060	0.040
FOX-7 sample 3 (aged)	0.23	0.15
Graphite sample 1 (NMP treated)	$(2.06 \times 10^{-4}$ mmol$)^1$	0.101

^{1}In 20 mg sample.
^{2}Washed with dioxan-MeOH (1–4 by volume) and then MeOH.
^{3}Two different samples of recrystallized FOX-7.

during the course of extended aging at 20°C and at 100°C (see Experimental section) was monitored (Tables 2 and 3). Before sealing the samples in the vials, they were washed with methanol to ensure that there was no surface contamination. All samples released some NMP on initial aging at 20°C (7 days), but TATB released much less than the other three samples, even though it was known to contain a comparable amount of NMP. Heating at 100°C released more NMP, but again TATB retained more than the other samples. The samples were then rewashed to remove any surface contamination that had been generated and then resealed and subjected to further

Table 2
NMP/argon ratios at various stages during aging

	Sample (NMP/argon ratio)[1]				
Treatment	TATB	HNS fine	HNS coarse	FOX-7	Graphite
Freshly washed	0.00000	0.0987	0.0889	0.0740	
7 days at 20°C	0.00030	0.0433	0.4612	0.2627	
2 hr at 100°C	0.00102	0.1390	0.5531	0.5336	0.00127
Rewashed	0.00000	0.0008	0.0246	0.0001	
12 days at 20°C	0.00049	0.0016	0.0722	0.0020	
7 days at 20°C	0.00125	0.0022	0.0578	0.0024	
7 days at 20°C	0.00000	0.0009	0.0168	0.0000	
8 days at 20°C + 2 hr at 100°C	0.00148	0.0064	0.0615	0.0040	

[1] The NMP/argon ratio for the head-space above liquid NMP was 4.72.

Table 3
NMP/argon ratios for TATB during aging at 100°C

Treatment/min at 100°C	NMP/argon ratio
20	0.00298
40	0.00349
60	0.00353
80	0.00403
100	0.00397
120	0.00419

aging. The amount of NMP released during this second aging sequence was significantly lower for all samples except TATB. Finally, the samples were removed from the vials and reanalyzed by NMR. This gave an indication of what proportion of the initial NMP had been lost during the extended aging. The data in Table 1 indicate that this loss was only 6% for TATB (TATB sample 3), 47% for fine HNS (HNS sample 4), 61% for coarse HNS (HNS sample 5), and 12% for FOX-7 (FOX-7 sample 3). It is clear that occluded NMP cannot be removed by aging, even at 100°C. It is also evident that head-space

GC-MS can give a misleading indication of the amount of contamination. The amount of NMP in the head-space during the second aging sequence of some of the samples (HNS, FOX-7) might suggest that there was little NMP in the sample, but the final NMR analysis demonstrated that this was not the case.

It has been reported [9] that solvent (dimethylformamide, DMF) trapped in HNS IV may be removed by washing with a mixture of dioxan and methanol (1–4 by volume). We found that this method also worked for the removal of essentially all of the NMP from HNS IV (see Table 1, HNS IV sample 2). However, application of the same method to HNS recrystallized from NMP (fine and coarse) was less successful, only about 80% of the NMP being removed from fine HNS (HNS sample 6), and 60% from coarse HNS (HNS sample 7).

The removal of NMP from contaminated samples was also attempted using sonication. A suspension of the material in 5% methanol-water (3–5 g/100 ml) was sonicated in an ultrasonic bath during 2 hr and then recovered and analyzed by ^{1}H NMR spectroscopy (see Table 1). This demonstrated that some of the NMP had been removed, viz., 12% from TATB (TATB sample 2), 48% from HNS (coarse only, HNS sample 3), and 76% from FOX-7 (FOX-7 sample 2).

It is clear that for all of the explosive materials studied, most of the NMP does not lie near the surface of the crystals and is not easily removed by either washing or heating. It must therefore occupy sites deep within the crystal structure. For TATB and FOX-7, both of which have layered crystal structures (interplanar distance ~ 0.6 and ~ 0.3 nm, respectively) similar to that of graphite (interplanar distance 0.34 nm), intercalation is probably involved, with the NMP molecules (shortest cross-sectional distance ~ 0.2 nm) residing in the interplanar layers. For HNS, the NMP most probably resides at defect sites within the crystal structure.

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