Full Paper

Identification of Blue Discoloration in PBX 9404 using Ultrahigh Pressure Liquid Chromatography with Quadrupole Time-of-Flight Mass Spectrometry

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Abstract: PBX 9404, composed of 94 wt% HMX (1,3,5,7-Tetranitro-1,3,5,7-tetrazoctane), 3 wt% NC (nitrocellulose), 2.9 wt% CEF (tris(beta-chloroethyl) phosphate) and 0.1 wt% DPA (diphenylamine), has often been observed with a slight to entire blue discoloration of the manufactured prills. This blue discoloration has been observed since the formulation development of PBX 9404 in the late 1950s. In order to determine the source of the blue discoloration in PBX 9404, ultraviolet/visible (UV/Vis) absorbance of PBX 9404 and two potential candidates for the discoloration, p-nitrosodiphenylamine (p-NDPA) and N-nitrosodiphenyl-amine (N-NDPA) were evaluated. An absorbance band at 590 nm in PBX 9404 sample was attributed to the blue discoloration while p-NDPA and N-NPDA had different absorbance bands. Using the knowledge gained from the UV/Vis analysis, a semi-targeted approach using ultrahigh pressure liquid chromatography coupled to UV/Vis detector and quadrupole time of flight mass spectrometry (UHPLC-UV/Vis-QTOF) was implemented. Investigating the UHPLC-UV/Vis-QTOF chromatograms at a wavelength of 590 nm, a single compound was tentatively identified as being the source of the blue discoloration. Targeted tandem mass spectrometry (MS/MS) on the compound and subsequent analysis indicated that 4,4′-{[4-(Phenylimino)-2,5-cyclohexadien-1-ylidene]methylene}bis(N-phenylaniline), also known as Spirit Blue Base, was the source of the blue discoloration, which was confirmed using a standard. A theory on the formation of Spirit Blue Base in PBX 9404 involving DPA, nitric acid (HNO_3) / nitrogen oxide(s) NO_x, and formaldehyde is proposed.

Keywords: PBX 9404 · UHPLC-QTOF · Diphenylamine · Spirit Blue Base

1 Introduction

One of the first plastic bonded explosives (PBXs) developed at the Los Alamos Scientific Laboratory (now Los Alamos National Laboratory) was PBX 9404, which first was qualified for use in the mid-1950's. Requiring an extremely high energy density, PBX 9404 is composed of 94 wt% HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazoctane), with an energetic binder system containing 3 wt% NC (nitrocellulose), 2.9 wt% CEF (tris(beta-chloroethyl) phosphate), and 0.1 wt% DPA (diphenylamine). After its initial formulation, PBX 9404 molding powder is an off-white color, but will change to various colors depending on the lot and storage conditions with the most common color being blue (which occurs within the first couple of days after formulation) [1]. Numerous researchers have theorized the source of the blue discoloration in PBX 9404 is from the reaction of DPA with decomposition products of NC [1,2]; however, minimal research has been performed evaluating DPA and NC decomposition in PBXs. Because of notable accidents attributed to the formulation's mechanical and sensitivity properties as well as the low thermal stability of the NC binder system, PBX 9404 is no longer used [3,4]. In fact, in analysis of the time vs temperature to achieve 3 wt% decom-position of the NC/CEF + DPA binder system, it was found that at 50 °C this period was only 0.34 years and at 120 °C it was reduced to 0.5 hours [4]. Despite the decades of observation of this colorization effect in PBX 9404, the actual mechanism and species involved has remained a mystery.

Decomposition of DPA in the presence of nitro-containing compounds in propellants (most notably those containing NC) has been widely studied using a variety of techniques [5–9]. Indeed, work has even been done to model decomposition kinetics of NC and DPA degradation products [7,10]. Most work focused on DPA reacting with NO_x or HNO_x to form nitroso or nitro DPA derivatives with a large focus on N-nitrosodiphenylamine. However, several researchers have observed a blue discoloration when aging

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DPA in the presence of nitro-containing compounds and concluded that it was likely not a nitroso or nitro DPA derivative, but they were unable to determine an identity of the chemical species [6,11]. In order to determine trace decomposition products, ultrahigh pressure liquid chromatography coupled to a UV/Vis detector and quadrupole time-of-flight mass spectrometry (UHPLC-UV/Vis-QTOF) was utilized and subsequently a mechanism of formation proposed. While this observation is limited to PBX 9404, it stands to reason that a similar mechanism could be seen in other explosive-based materials that use DPA as a stabilizer.

2 Experimental Section

2.1 Explosive

A library standard of PBX 9404, Lot 602-5, was obtained from storage magazines at Los Alamos National Laboratory (Figure 1). This sample was manufactured in by Holston Army Ammunition Plant in 1971.

2.2 Chemicals

Acetonitrile (HPLC Plus), dichloromethane (HPLC Plus), and sulfuric acid (99.999%) were obtained from Sigma-Aldrich. Ammonium acetate was obtained from VWR and was diluted to 10 mM using deionized water obtained from Sigma-Aldrich. p-nitrosodiphenylamine (p-NDPA) was purchased from TCI America and N-nitrosodiphenylamine (N-NDPA) was purchased from Sigma-Aldrich. Opal Blue SS (Spirit Blue) was purchased from Fisher Scientific.

Figure 1. Sample of PBX 9404 prills showing the intense blue discoloration.

2.3 Instrumentation

2.3.1 Ultraviolet/Visible (UV/Vis) Absorbance Analysis

The PBX 9404 sample was prepared by dissolving ~200 mg in 20 mL of dichloroethane. The solution was then filtered through a 25 mm diameter Whatman Puradisc 25TF filter (GE Healthcare, Marlborough, MA, USA) containing a 0.45 µm PTFE membrane in a polypropylene housing. p-NDPA and N-NDPA were prepared by dissolving ~5 mg of sample in ~10 mL of dichloroethane. The UV/Vis absorbance spectrum was collected on a HP 8453 with quartz cuvettes with a path length of 0.1 cm. A blank was measured using dichloroethane solution prior to collection of the PBX 9404, p-NDPA, and N-NDPA spectra. The resulting data was exported as a text file and then imported into Matlab 2019a (Mathworks, Inc., Natick, MA, USA) for visualization.

2.3.2 Ultrahigh Performance Liquid Chromatography with Quadrupole Time of Flight Mass Spectrometry (UHPLC-QTOF)

The PBX 9404 sample was prepared by dissolving ~180 mg of sample in ~3 mL of dichloromethane. The sample was swirled until the prills appeared to have decomposed and a white powder (HMX) was visible on the bottom of the dram vials. The solution was then filtered through a 25 mm diameter Whatman Puradisc 25TF filter containing a 0.45 µm PTFE membrane in a polypropylene housing. The sample was then analyzed via a Shimadzu UHPLC system (Shimadzu, Japan) coupled to a SCIEX X500R QTOF (SCIEX, Framingham, MA, USA). The UHPLC system consisted of two binary pumps (LC30-AD), degasser (DGU-30 A), column oven (CTO-30 A), autosampler (SIL-30 A), and UV-Vis detector (SPD-30 A). The UV-Vis detector collected wavelengths from 200–700 nm with a slit width of 8 nm at a rate of 6.25 Hz. The QTOF system was equipped with an atmospheric pressure chemical ionization (APCI) source that was operated in positive mode. The APCI conditions were as following: ionspray voltage 5.5 kV, temperature 300 °C, ion source gas #1 551.6 kPa, ion source gas #2 551.6 kPa, declustering potential 80 V, and CAD gas 7 a.u. The instrument was run in data-independent acquisition, which collected TOFMS spectra 100–2000 m/z at an accumulation time of 0.25 seconds and a collision energy of 10 V (minimum value). The top 5 most intense m/z that had a minimum intensity threshold of 10 counts/second per scan were then selected for tandem mass spectrometry (MS/MS). For MS/MS mode, mass channels 40–2000 were collected at an accumulation time of 0.1 seconds. The collision energy was set to −80 V.

Separations were carried out on a Phenomenex (Torrence, CA, USA) Kinetex C_{18} column (100 mm ×3.0 mm, 1.7 µm). The injection volume was 5 µL, and the column oven was set to 40 °C with a flow rate of 1.0 mL/min. The

mobile phase composition consisted of 10 mM ammonium acetate (A) and acetonitrile (B). The gradient program was: 0 min, isocratic at 0% B; 0–10 min, linear gradient to 100% B; 10–15 min isocratic at 100% B. The UHPLC-UV/Vis-QTOF system was controlled by SCIEX OS 1.6.1 software, and the subsequent data processing was performed using this same software. The relevant data was exported as a text file and then imported into Matlab 2019a for visualization.

3 Results and Discussion

3.1 UV/Vis Absorbance Results

In order to help hone in on the correct chemical prior to analysis via UHPLC-UV/Vis-QTOF, a simple analysis of PBX 9404 and two potential compounds responsible for the discoloration, p-NDPA and N-NDPA, using UV/Vis absorbance was undertaken. Based on prior literature, p-NDPA and N-NDPA have been identified as decomposition products of diphenylamine and as potential sources of the discoloration. Figure 2A and 2B shows the UV/Vis absorbance spectra for PBX 9404 and p-NDPA and N-NPDA, respectively. PBX 9404 exhibits a large, broad absorbance band at 230 nm which is attributed to the HMX and nitrocellulose and an additional absorption band at 590 nm, which is why the solution of PBX 9404 appears blue. p-NDPA has absorption bands at 233 and 290 nm while N-NDPA has a single absorption band at 412 nm.

Additionally, spectra of p-NDPA and N-NDPA were obtained in acidic solution (2 drops of sulfuric acid were to the solutions) because the spectra of nitroso-containing compounds are known to shift due to the protonation of the nitroso group. While the absorption bands for p-NDPA and N-NDPA did shift to longer wavelengths (not shown for brevity), the spectra did not match that of PBX 9404. Thus it was concluded that these two compounds were likely not the source of discoloration in PBX 9404.

3.2 UHPLC-QTOF Results

UHPLC-UV/Vis-QTOF generates an immense amount of information and it would be nearly impossible to comb through the entire dataset in order to find the chemical species responsible for the blue discoloration. Using the knowledge gained from the UV/Vis analysis of PBX 9404, a semi-targeted approach was undertaken. The resulting UV/Vis chromatogram from the analysis of PBX 9404 for 590 ± 2.5 nm, shown in Figure 3, was investigated to identify compounds which were most likely responsible for the blue discoloration. Only a single compound with a retention time of ~9.15 minutes was identified as being the compound likely for the blue discoloration.

Tandem mass spectrometry (MS/MS) was performed on this compound targeting the associated m/z (m/z 516) in
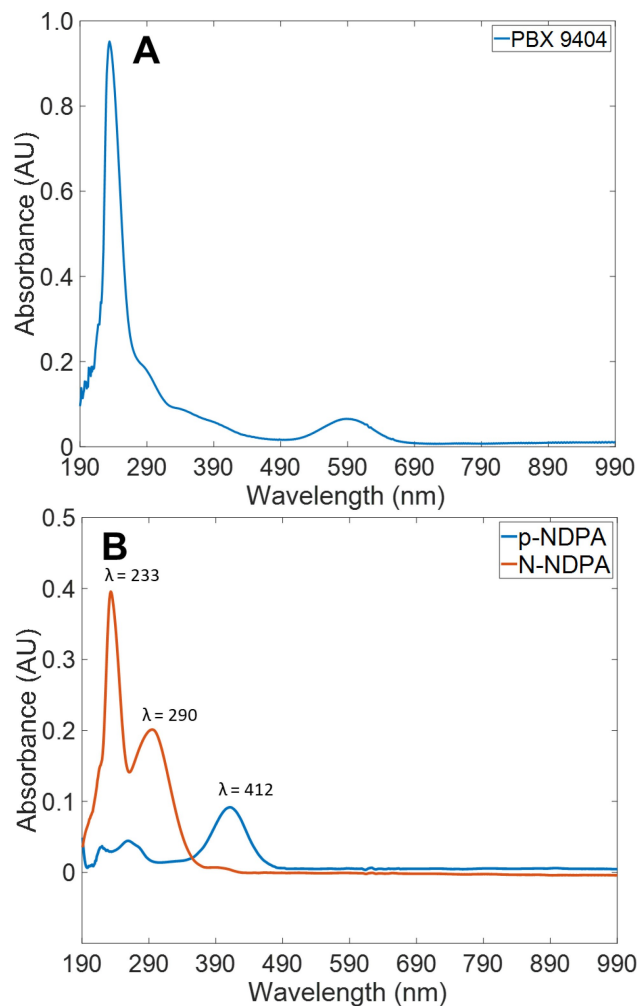

Figure 2. UV/Vis Spectra for PBX 9404 (**A**) and p-nitrosodiphenylamine (p-NDPA) and N-nitrosodiphenylamine (N-NDPA) (**B**).

order to aid in the identification. Using the built-in compound identification tools in SCIEX OS, a chemical formula was identified and forwarded to ChemSpider (http://www.chemspider.com) and was tentatively identified as 4,4′-{[4-(Phenylimino)-2,5-cyclohexadien-1-ylidene]methylene}bis(N-phenylaniline) also known as Spirit Blue Base.

In order to confirm the identification, a standard of Opal Blue SS (the cationic salt), was evaluated using the same UHPLC-UV/Vis-QTOF methodology as for PBX 9404. The standard eluted at the same retention time, had the same λ_{max}, same parent m/z, and identical MS/MS spectrum, thus it was concluded that Spirit Blue Base is the compound responsible for the blue discoloration in PBX 9404. Figure 4 shows a "head-to-toe" plot comparing the MS/MS spectrum from PBX 9404 and the standard Opal Blue SS.
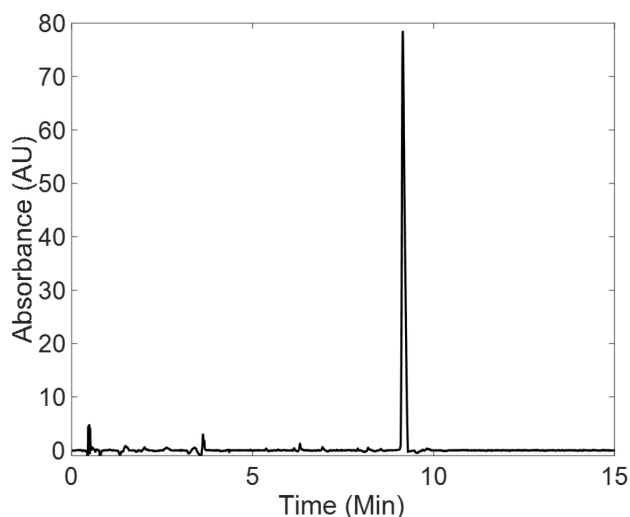
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Figure 3. UV/Vis chromatogram for the analysis of PBX 9404. Wavelength 590 ± 2.5 nm is shown. A single compound was identified as potential source for the blue discoloration.
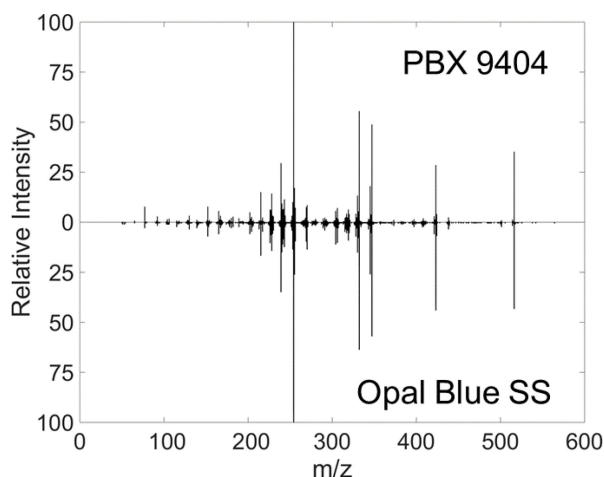

Figure 4. "Head-to-toe" plot of the MS/MS spectra of the tentatively identified compound from PBX 9404 and the Opal Blue SS standard.

3.3 Theory on Formation

For PBX 9404 to produce Spirt Blue Base, we theorize that certain chemical species must be present in the material. The three chemical species that are key for the synthesis of Spirt Blue Base are formaldehyde, nitric acid/NO$_x$ gas, and diphenylamine. Diphenylamine is already present in the material as a stabilizer. Two possible sources of formaldehyde include residual material leftover from the synthesis of the explosive HMX or decomposition of HMX [12]. However, HMX decomposes at ~235 °C thus is unlikely the cause since the discoloration is observed in freshly manufactured prills which were stored at room temperature. The most likely source of formaldehyde is from the decomposition of

nitrocellulose, which does occur at much lower temperatures [13]. Nitric acid/NO$_x$ gases are common decomposition products of nitrate ester based explosives such as nitrocellulose [14, 15]. With the reasonable expectation that these three materials are present in PBX 9404, we propose a potential pathway for how this material is formed.

Synthesis of Spirit Blue Base, like many triamino-triarylmethane dyes, can be performed through a condensation reaction of formaldehyde and the appropriate aryl amine [16]. The first step proposed is an acid-catalyzed electrophilic aromatic acylation of the para position of diphenylamine with formaldehyde. This reaction produces a benzoyl alcohol derivative of diphenylamine (Scheme 1).

Following this electrophilic aromatic addition, the newly formed benzoyl alcohol is oxidized to the benzaldehyde derivative (Scheme 2). Literature reports [17–20] have shown that benzoyl alcohols can be oxidized to the corresponding benzaldehyde using nitric acid in the presence of nitrites (NO$_2$).

After oxidation, another acid-catalyzed electrophilic aromatic acylation can occur, producing the alcohol intermediate, followed by a condensation reaction with a third equivalent of diphenylamine resulting in the triamino-triarylmethane substrate seen in Scheme 3. Similar reactions have been reported to occur when synthesizing triamino-triarylmethane dyes, for example crystal violet [16].
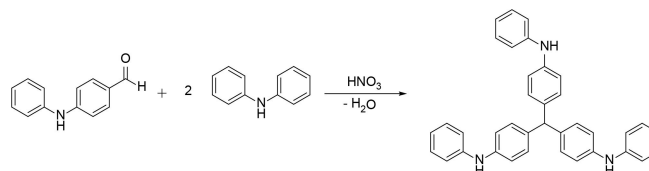
Finally, the two-electron oxidation of the triamino-triarylmethane leads to the cationic Spirt Blue dye. The most likely oxidant present in the material is the NO$_x$ gas generated from the decomposition of nitrocellulose (Scheme 4).
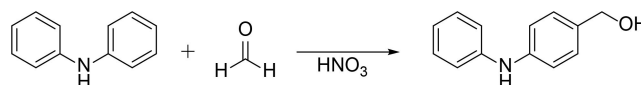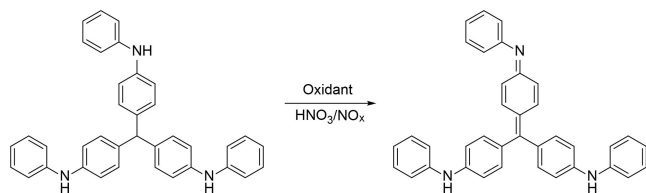

Scheme 1. Proposed synthesis of 4-(Hydroxymethyl)phenylphenylamine.
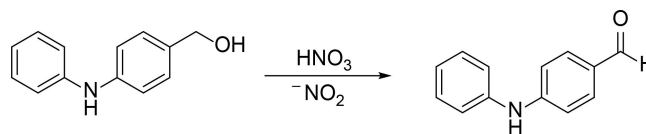
Scheme 2. Proposed synthesis of 4-(phenylamino)-benzaldehyde.

Scheme 3. Proposed synthesis of 4,4',4''-methylidynetris[N-phenyl-Benzenamine.

Scheme 4. Proposed synthesis of Spirt Blue Base.

4 Conclusion

Blue discoloration in PBX 9404 has been observed since its initial formulation in the 1950s but the chemical compound responsible for its discoloration had never been identified. Herein, through use of UV/Vis absorbance, the absorption band responsible for the blue discoloration was identified. Using a semi-targeted UHPLC-UV/Vis-QTOF analysis and with confirmation using a standard, Spirit Blue Base was identified as the compound responsible for the discoloration. Additionally, a theory on the formation of the Spirit Blue Base was provided.

Acknowledgements

Data Availability Statement

No Data available.

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