Studies on 2,4,6-trinitrophloroglucinol (TNPG)—A novel flash sensitizer

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2,4,6-Trinitrophloroglucinol (TNPG), useful for percussion caps, detonator formulations and dye manufacture, has been synthesized with conventional nitrating agents under mild reaction conditions. The compound is characterized by IR, NMR, mass and elemental analyses. Further, the purity of the compound is confirmed by estimation of nitro groups. Thermal and explosive properties of TNPG have been investigated. The detonation velocity and detonation pressure are also estimated.

Experimental Procedure

Melting point was determined on open capillary and are uncorrected. The IR spectrum was recorded on a Perkin-Elmer infrared spectrometer using KBr matrix. NMR spectra were recorded on Brucker-300 MHz using acetone-d$_6$ as solvent and chemical shifts were reported in $\delta$ units with reference to tetramethylsilane (TMS) as internal standard. Elemental analysis was performed on Carlo-Erba Elemental Analyzer EA-1108. Mass spectrum was determined by electron ionization of 70 eV on a mass spectrometer using direct insertion technique, Deflagration temperature was determined in Wood's Metal bath, while differential thermal analysis (DTA) was recorded by heating 10 mg of sample at a rate of 10°C/min in the presence of static air. The loss in weight versus temperature was measured by thermogravimetric analysis (TGA), and moisture content was determined by using Karl Fischer apparatus. The purity of TNPG was determined by nitro group estimation using TiCl$_3$ - ferric alum method. The impact sensitivity was determined by Fall Hammer Method using 2.0 kg drop weight and friction sensitivity was determined on Julius Peter's apparatus by following a standard method. The velocity of detonation and detonation pressure were calculated by methods reported in the literature.

Materials

Phloroglucinol dihydrate (m.p. 218 - 220°C) was obtained from Aldrich Chemical Company, USA and used as a starting material, while mixture of concentrated nitric acid and sulphuric acid SQ Grade, Quali-
gens, was used as a nitrating mixture. The hydrochloric acid was also SQ Grade, Qualigens.

**Synthesis**

To a one-litre three-necked round-bottomed flask fitted with mechanical stirrer, separating funnel and thermometer placed in a plastic tube, 50 mL of concentrated sulphuric acid was transferred carefully. To this, phloroglucinol dihydrate (10 g, 0.061 mol) was added slowly with continuous stirring till dissolved. The temperature of phloroglucinol solution was brought down to 0°C with the help of a ice-salt mixture and at this temperature, the precooled nitrating mixture consisting of 100 mL of conc. H₂SO₄ and 100 mL of nitric acid (sp. gravity 1.3) was added dropwise to the reaction flask under stirring for about 45 min. After complete addition of nitrating mixture, the reaction mixture was stirred for 1½ h at 0°C followed by 1 h at ambient temperature. The reaction mixture was filtered through Buchner funnel using glass cloth and washed thoroughly with cold dilute hydrochloric acid and finally dried at 60°C in water jacketed oven, yield, 10.5 g (~61%).

The product thus obtained was crystallised from dilute hydrochloric acid.

- m.p. 166-167°C; DTA: 167°C (Endotherm) and 192°C (Exotherm).
- IR (KBr) cm⁻¹: 1637, 1585, 1531, 1359, 1321 and 810 (NO₂ scissor)
- ¹H NMR (Acetone-d₆/TMS) δ ppm: 9.5 (s, 3H, OH)
- ¹³C-NMR (Acetone-d₆/TMS) δ ppm: 152 (s, 3C, C-NO₂), 122 (s, 3C, C-OH)
- EIMS (70 eV) m/z : 261 (M⁺ - H₂O, 100%), 243 (M⁺ - 2H₂O, 5%), 231 (261 - NO, 8%), 213 (243 - NO, 10%), 169 (261 - 2NO₂, 5%), 157 (261 - NO - NO₂, - CO, 15%), 113 (157 - CO - O, 34.35%), 95 (261 - 3NO₂ - CO, 15.1%), 94 (157 - HNO₃, 14%), 70 (157 - 2CO - HNO, 24.1%).
- Anal. Calcd. for C₆H₅N₃O₁₀ (Mol. Wt. 279): C-25.80; H- 1.79; N- 15.05
- Found : C- 25.67; H- 1.71; N- 14.86.

**Results and Discussion**

2,4,6-Trinitrophloroglucinol (TNPG) was prepared from phloroglucinol dihydrate through a mild nitration procedure:

\[
\text{Phloroglucinol dihydrate} \rightarrow 2,4,6-\text{Trinitrophloroglucinol monohydrate (TNPG)}
\]

The reaction is very sensitive towards concentration of nitric acid as well as temperature. Therefore, nitric acid of specific gravity (1.3) was taken and temperature of reaction was maintained at 0°C which results TNPG of high purity and in good yields. TNPG is a dark yellow crystalline material with a melting point of 166-167°C which has been characterized by spectral data and elemental analysis.

The IR spectrum of TNPG shows the absence of −OH absorption, thus supplementing the opinion that all the hydroxyl groups are completely chelated with the nitro groups. It is also interesting to note that the lack of absorption at 1724-1695 cm⁻¹ suggests the absence of carboxyl group in the structure which is perhaps due to keto-enol equilibrium of TNPG.

Further, −C=O stretching frequencies appear at 1637 and 1585 cm⁻¹ while asymmetric and symmetric vibrations of −NO₂ group absorb at 1531 and 1359 cm⁻¹ respectively. The C-O-H bending appears at 1425 cm⁻¹, -C=O-O- out of plane absorbs at 1321 cm⁻¹ and hexasubstituted benzene absorbs at 453 cm⁻¹.

In ¹H NMR, the hydroxyl protons resonate at δ 9.5 while ¹³C NMR shows two strong singlets at δ 152 and δ 122. The electron impact mass spectroscopy (EIMS) was carried at 70 eV and the fragmented species (Scheme 1) further confirms the structure. The loss of m/z 18 (H₂O) from the parent molecule produces m/z 261 with weak abundance, i.e., TNPG (anhydrous) which undergoes further fragmentation to produce diagnostics ions with rich relative intensities of m/z 157, 113, 95, 94 and 70. The observed elemental analysis data of TNPG are in excellent agreement with the calculated values.

The analysis of TNPG was further carried out by Karl-Fischer Apparatus, nitro group estimation and TGA. The results obtained are summarized in Table 1. The moisture content of TNPG (as determined by Karl-Fischer Method) was found ≈ 6.5% (Table 1). Also the TGA data shows that the loss of water molecule takes place at ≈110°C and the "weight loss" ≈ 6.65 to 6.89% corresponds to one molecule of
"water of crystallization". This clearly brings out that TNPG is monohydrate in nature.

This is supported by the nitro group estimation data of TNPG using TiCl₃/ferric alum method where purity of TNPG was obtained in the range of 98.9 - 99.7% according to the following equation:

\[
\% \text{ of purity of TNPG.H₂O} = \frac{(V_2 - V_1) \times f \times 0.0031}{\text{Mass of sample}}
\]

where, \( V_2 \) is the volume in mL of 0.2 N ferric alum required for blank titration, \( V_1 \) is the volume in mL of 0.2 N ferric alum required for the unreacted titanous-

chloride in experiment and \( f \) is the factor for 0.2 N ferric alum.

TNPG was evaluated for thermal and explosive properties and the results obtained are presented in Table 2. The DTA thermogram (Fig.1) consists of an endotherm at 167°C corresponding to melting point of TNPG and a strong exotherm at 192°C indicating its exothermic decomposition. TNPG deflagrates at 192°C which is supported by a strong exotherm in DTA. The study of explosive properties of TNPG (Table 2) reveals that it is quite sensitive to impact and its "height for 50% explosion" is 36 cm. Further, "Figure of Insensitiveness (F of I)" is 28. The friction sensitivity data indicates that TNPG does not explode/ignite up to 36 kg. Thus, the impact and friction sensitivities data infers that TNPG is very prone to hot spot formation, while it is safe to friction. The insensitivity towards friction may be supported by the fact
that hydroxyl groups present in TNPG molecule are completely hydrogen bonded with the nitro groups. The predicted performance parameters like velocity of detonation (VOD) and detonation pressure (DP) are comparable to that of pentaerythritol tetranitrate (PETN), a well known secondary explosive used in detonators as base charge and also in detonating cord. Due to high VOD of TNPG (~ 8053 m/s), sensitivity towards impact and overall performance, it is being used in basic lead azide/lead styphnate/aluminium (BLASA) composition as a flash sensitizer.

Conclusions

Trinitrophloroglucinol has been synthesized and fully characterized. The 'loss in weight' data reveals that TNPG contains one molecule of 'water of crystallization'. The properties of the compound are very attractive and thus, it is a useful ingredient for priming and detonating compositions.

References

1 Fredrich W, Ges Z & Schiess U, Spengstoffw, 80 (1933) 113.
2 Rathsburg H, Brit Pat, 190215; 190844, (1921); Angew Chem., 41 (1928) 1285.
3 Benedikt R, Ber, 11 (1878) 1376.