

Synthesis, characterization, thermal and explosive properties of potassium salts of trinitrophenol

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Abstract

Three different substituted potassium salts of trinitrophenol (H_3TNPG) were prepared and characterized. The salts are all hydrates, and thermogravimetric analysis (TG) and elemental analysis confirmed that these salts contain crystal H_2O and that the amount crystal H_2O in potassium salts of H_3TNPG is 1.0 hydrate for mono-substituted potassium salts of H_3TNPG [$K(H_2TNPG)$] and di-substituted potassium salt of H_3TNPG [$K_2(HTNPG)$], and 2.0 hydrate for tri-substituted potassium salt of H_3TNPG [$K_3(TNPG)$]. Their thermal decomposition mechanisms and kinetic parameters from 50 to 500 °C were studied under a linear heating rate by differential scanning calorimetry (DSC). Their thermal decomposition mechanisms undergo dehydration stage and intensive exothermic decomposition stage. FT-IR and TG studies verify that their final residues of decomposition are potassium cyanide or potassium carbonate. According to the onset temperature of the first exothermic decomposition process of dehydrated salts, the order of the thermal stability from low to high is from $K(H_2TNPG)$ and $K_2(HTNPG)$ to $K_3(TNPG)$, which is conform to the results of apparent activation energy calculated by Kissinger's and Ozawa–Doyle's method. Sensitivity test results showed that potassium salts of H_3TNPG demonstrated higher sensitivity properties and had greater explosive probabilities.

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1. Introduction

Many aromatic compounds with nitro groups on the ring are useful explosives. Trinitrophenol (2,4,6-trinitro-1,3,5-benzenetriol, H_3TNPG) can serve as an explosive and an important intermediate in the synthesis of several other explosives. Salts of trinitrophenol are useful as initiator compositions [1–7]. Our laboratory has been interested in the structure and properties of polynitrohydroxybenzenes for several years. The potassium salt of aromatic compounds with nitro groups is more stable and less impact sensitive than the parent compound. Potassium energetic materials are emphasized for no heavy metal pollution and their explosion capacity is corresponding or prior to the common primary explosives, which

has been used in primary explosive and initiator compositions, with recent emphasis on its environmental advantages over materials that contain heavy metals [8–12]. Their properties and parameters are interesting and important from the standpoint of technology and/or safety; however, they have not been sufficiently presented in currently accessible information sources so far. The potassium salts of trinitrophenol ($K-H_3TNPG$) are highly unstable metallic salts of polynitrohydroxybenzenes, which would cause serious explosive accidents during their production, isolation, handling and further treatment.

We have previously published or presented crystal structure of salts of polynitrohydroxybenzenes [13–17]. The present paper focused on our previous work, is particularly focused on the basic stability characteristics of the compounds studied (i.e. on their resistance to thermal reactivity and explosive decomposition) and it does not ignore some of the other physicochemical data of the compounds studied. The compounds were characterized and subjected to sensitivity tests to assess their hazardous nature. The synthesized $K-H_3TNPG$ salts were subjected to thermal studies in differential scanning calorimetry and ther-

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mogravimetry differential thermal analyzer. Kinetic parameters, impact, friction, and flame sensitivity data were determined to assess their potential application as promising ingredients of various pyrotechnic compositions.

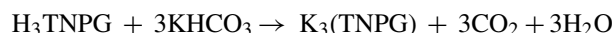
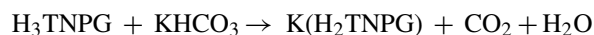
2. Experimental

2.1. Materials

H₃TNPG was synthesized according to the procedure reported in literature [18]. Potassium hydrocarbonate (KHCO₃) was analytic grade.

2.2. Preparation of K-H₃TNPG

H₃TNPG was dissolved in water, and solid calculated amount of KHCO₃ was added. The mixture was heated to boiling for 40 min at 60–80 °C and then allowed to cool slowly. K(H₂TNPG), K₂(HTNPG), and K₃(TNPG) were obtained as yellow, orange-yellow, and red needles, respectively, which were washed with cold water and ethanol, and dried under vacuum at 60 °C for 3–4 h. They were analyzed by elemental analyses, FT-IR and TG technique. The preparation was carried out according to the following general scheme:



2.3. Apparatus and conditions

In the present experiments, the carbon, nitrogen, and hydrogen analyses were performed on a Flash EA 1112 full-automatic trace element analyzer.

The FT-IR spectra of K-H₃TNPG and their thermal decomposition residua were recorded on a Bruker Equinox 55 spectrometer (KBr pellets) in the range of 4000–400 cm⁻¹ at 4 cm⁻¹ resolution.

DSC was made on a CDR-4P differential scanning calorimeter (Shanghai Tianping Instrument Factory, China) with an aluminium crucible. The operation conditions are as follows: sample mass is less than 0.5 mg, heating rates are 5, 10, 15, 20, and 25 °C min⁻¹, respectively, from 50 to 500 °C, atmosphere is a self-generating static atmosphere, reference sample is α-Al₂O₃.

TG measurements were made using Perkin-Elmer Pyris-1 thermogravimetric balance with a platinum pan. The operation conditions are as follows: sample mass is less than 0.5 mg, heating rates is 10 °C min⁻¹ from 50 to 500 °C, atmosphere is dry nitrogen as atmosphere with a pressure of 0.2 MPa.

2.4. Sensitivity characterization

The sensitivity of the synthesized compounds to impact stimuli was determined by Fall Hammer. Apparatus using 0.8 kg

drop weight and 20 mg sample and height for 50% probability of explosion (*h*₅₀) was determined statistically [19].

The friction sensitivity of the compounds was determined on a model MGY-1 pendular friction sensitivity apparatus by applying a standard method. In this test, 20 mg sample was compressed between two steel poles with mirror surfaces at the pressure of 0.64 MPa, and was hit horizontally with a 1 kg hammer from 50° angle, the firing rate is obtained [19].

The flame sensitivity was tested on a model HGY-1 flame sensitivity apparatus. The testing condition is that quantity of the compound is (20 ± 2) mg and pressure 39.2 MPa [19]. Height for 50% probability of ignition (*h*₅₀) was determined statistically [19].

3. Results and discussion

3.1. Structure identification of K-H₃TNPG

The elemental analysis results on potassium salts of trinitrophenol are listed in Table 1. They are in good agreement with the formulae: K(H₂TNPG)·H₂O, K₂(HTNPG)·H₂O and K₃(TNPG)·2(H₂O) proposed for these salts. All the formulae show the presence of water molecules.

Fig. 1 shows the infrared spectra of K(H₂TNPG)·H₂O, K₂(HTNPG)·H₂O and K₃(TNPG)·2(H₂O) and their decomposition residua at various temperatures. The IR spectra demonstrated intensive and wide absorption bands are certainly indicative of water presented in the salts. The IR spectrum of H₃TNPG demonstrates, in addition to stretch vibrations of O–H bonds (3400–3600 cm⁻¹), three strong absorption groups in the ranges of 1636–1530 cm⁻¹ (stretch vibrations of C=C bonds and asymmetric stretch vibrations of nitro-groups, ν C=C and ν_{as} NO₂), 1360–1323 cm⁻¹ (symmetric stretch vibrations of nitro-groups, ν_s NO₂), and 1210–1155 cm⁻¹ stretch vibrations of C–O bonds, ν C–O) [3,18]. The formation of salts changes position and intensity of these absorption bands, however without any comprehensible regularity. It can be pointed out only that the first absorption band is shifted to a low-frequency area, 1607–1508 cm⁻¹. The other two absorption groups show a tendency to move towards each other: the tri-substituted salts demonstrated a wide multiple band at ~1280 cm⁻¹ instead of two absorption groups.

Table 1
Results of elemental analysis for K-H₃TNPG

Salts	Contents (%)			
	N	C	H	
K(H ₂ TNPG)·H ₂ O	Calculated	13.25	22.71	1.26
	Found	13.37	22.89	1.32
K ₂ (HTNPG)·H ₂ O	Calculated	11.83	20.28	0.85
	Found	11.95	20.32	0.96
K ₃ (TNPG)·2(H ₂ O)	Calculated	10.22	17.52	0.97
	Found	10.34	17.61	1.02

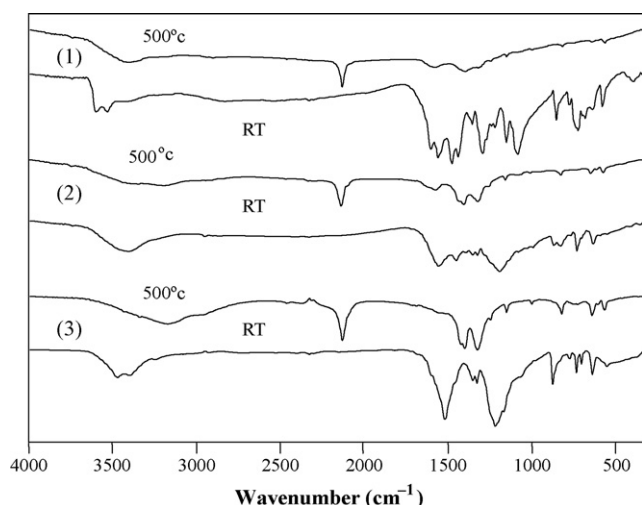


Fig. 1. IR spectra of K-H₃TNPG and their decomposition residues. (1) K(H₂TNPG)·H₂O; (2) K₂(HTNPG)·H₂O; (3) K₃(TNPG)·2(H₂O).

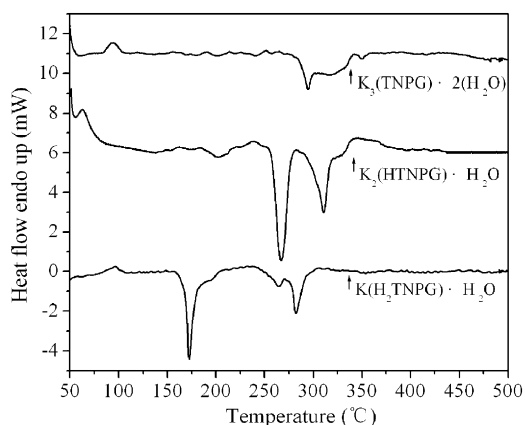


Fig. 2. DSC curves of K-H₃TNPG.

3.2. Mechanism of the thermal decomposition of K-H₃TNPG

Under linear temperature increase condition, DSC results obtained are depicted in Fig. 2 and TG results are given in Fig. 3. It can be seen from the curves that under the given conditions

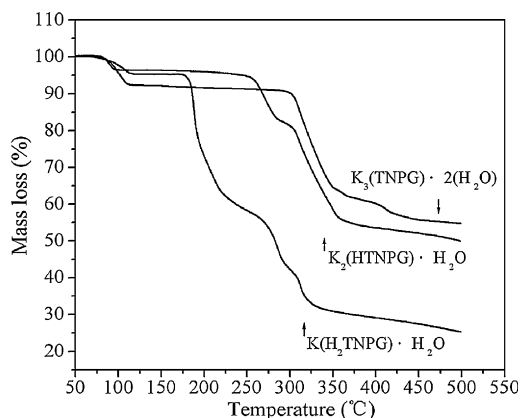


Fig. 3. TG curves of K-H₃TNPG.

the decomposition processes of these salts may be divided into two major stages: dehydration and exothermic process.

Their dehydration process appeared as only one step. DSC curves indicate that these processes are endothermic, and TG curves show that K(H₂TNPG)·H₂O lost mass 5.5% in the temperature range of 78.3–118.6 °C, K₂(HTNPG)·H₂O lost mass 5.3% in the temperature range of 78.3–118.6 °C and K₃(TNPG)·2(H₂O) lost mass 8.7% in the temperature range of 78.3–118.6 °C. These values of mass loss coincide with the theoretical values of 5.7, 5.1, and 8.8% very well.

The second stage is connected with the thermal decomposition of anhydrous K-H₃TNPG. K(H₂TNPG) exhibited two exotherms in the temperature range of 156–310 °C with the peak decomposition temperature (T_{max}) at 188.7 and 290.8 °C, respectively. The first exotherm at 156–219 °C is intense exothermic process. Further decomposition of the K(H₂TNPG) occurs at 246–310 °C, and other two main exotherms are exhibited in the DSC curve. Because two intense exothermic decomposition processes occur successively, one decomposition process does not finish, and another occurs. The mass loss corresponding to the two processes was 66%. K₂(HTNPG) exhibited two exotherms in the temperature range of 235–360 °C with the peak decomposition temperature (T_{max}) at 260.2 and 301.6 °C, respectively. For K₃(TNPG), the exotherm appeared in the temperature range of 270–320 °C with peak decomposition temperature (T_{max}) at 295 °C.

The total mass loss amounted to 74% for K(H₂TNPG), 49% for K₂(HTNPG), and 44% for K₃(TNPG) at 500 °C. The IR spectra of decomposed residues are shown in Fig. 2. The absorption band appears at 2240 cm⁻¹, which confirms that KCN was formed. Some new absorption bands appear at ~1470, ~1256, and ~827 cm⁻¹ for CO₃²⁻, which confirms that potassium carbonate are formed during decomposition processes. From the IR spectra of decomposed residues, the main decomposed production is KCN for K(H₂TNPG), KCN and K₂(CO₃) for K₂(HTNPG) and K₃(TNPG). The weight of solid residue is smaller for K(H₂TNPG), more for K₃(TNPG). This showed K(H₂TNPG) decomposition gave about heat and can decompose fully. Based on literature precedent [8], the thermal decomposition mechanism of K-H₃TNPG can be expected to proceed through elimination of NO₂ in anions to evolve abundant heat, followed by a breakdown of the benzene ring on heating.

Kissinger's and Ozawa–Doyle's method [20] were applied to study the kinetics parameters, based on the first exothermic peak temperatures measured from DSC curves at five different heating rates. The apparent activation energy E_k and E_o , pre-exponential factor A_k , and linear correlation coefficient R_k and R_o were shown in Table 2 (subscripts k and O denoted calculation results by Kissinger's method and Ozawa–Doyle's method, respectively). Their enthalpies ΔH were also calculated from DSC curves for a heating rate of 10 °C min⁻¹. The apparent activation energies for the first decomposed process are 249.9, 381.4, and 585.9 kJ mol⁻¹, respectively, obtained with the Kissinger's method. According to the onset temperature of the first exothermic decomposition process of dehydrated salts, the order of the thermal stability from low to high is

Table 2
Kinetic parameters and enthalpies of thermal decomposition of K-H₃TNPG

Salts	Heating rate (K min ⁻¹)	<i>T</i> _{max} (°C)	<i>E</i> (kJ mol ⁻¹)		ln <i>A</i> _K (s ⁻¹)	Linear correlation coefficient		ΔH (kJ mol ⁻¹)
			<i>E</i> _K	<i>E</i> _O		<i>R</i> _K	<i>R</i> _O	
K(H ₂ TNPG)·H ₂ O	5	184.3	249.9	244.9	26.62	-0.9989	-0.999	1001.7
	10	188.7						
	15	191.4						
	20	193.8						
	25	195.4						
K ₂ (HTNPG)·H ₂ O	5	256.8	381.4	371.2	35.76	-0.9967	-0.9968	705.2
	10	260.2						
	15	263.0						
	20	264.9						
	25	266.5						
K ₃ (TNPG)·2(H ₂ O)	5	292.2	585.9	566.2	52.42	-0.9953	-0.9955	1380.0
	10	295.0						
	15	296.6						
	20	298.1						
	25	299.6						

Subscripts K and O denoted calculation results by Kissinger's method and Ozawa–Doyle's method, respectively.

from K(H₂TNPG), K₂(HTNPG), to K₃(TNPG), which is conform to the results of apparent activation energy calculated by Kissinger's and Ozawa–Doyle's method. The tests show the thermal stability of potassium salts appeared to depend on the degree of substitution: the less metal atoms entered the molecule, the less the thermal stability.

3.3. Sensitivity of K-H₃TNPG

The sensitivity results are summarized in Table 3. These salts synthesized are sensitive towards mechanical stimuli. The sensitivity data obtained for the usually nitrophenol primary explosives, such as K(DNBF) and KPA under identical conditions is in close agreement with the reported data [21]. These materials may be classified under the hazard category. Hence, these materials need to be handled by experienced HEMS chemists/scientists/technologist during their synthesis, characterization, scale up, storage, transport, and evaluation. The unplanned initiation of these materials may cause mass explosion.

The sensitivity properties of K-H₃TNPG appeared to depend on the degree of substitution: the more metal atoms entered the molecule, the less the sensitivity. The sensitivity of these salts correlates with their thermal stability: the less the thermal stability, the higher the sensitivity. The results demonstrated that the more metal atoms entered the molecule, the less the mechanical sensitivity. M–O bond in the compounds is the weakest and

prone to initiate explosive, at the same time O–H bond is an initiating bond either. Flame sensitivity test showed that the flame sensitivity of K-H₃TNPG is strong, while K(H₂TNPG) is even stronger.

4. Conclusion

The potassium salts of trinitrophenol glucinol were prepared and characterized during this work. It was indicated by the research results that the thermal decomposition of these salts would be divided into two major stages, dehydration and exothermic process. According to the main decomposition peak temperatures, their thermal resistance decreases in the sequence: K₃(TNPG) > K₂(HTNPG) > K(H₂TNPG). The tests show the less metal atoms entered the molecule, the less the thermal stability. The sensitivity properties of K-H₃TNPG also appeared to depend on the degree of substitution, the more metal atoms entered the molecule, the less the sensitivity. The sensitivity of these salts correlates with their thermal stability. The tests obtained during this work show these compounds can be recommended for further investigations as components of clean initiating compositions and ignition.

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References

- [1] M.N. Sikder, A.K. Sikder, D.V. Survase, J.P. Agrawal, Studies on 2,4,6-trinitrophenol glucinol (TNPG)—a novel flash sensitizer, *Ind. J. Eng. Mater. Sci.* 11 (2004) 59–62.
- [2] W.F. Liu, V.P. Sinditskii, V.Y. Egorshv, Study on the burning velocity of lead trinitrophenol glucinate, *Initiators Pyrotech.* 3 (2003) 34–35.

Table 3
Results of sensitivity tests of K-H₃TNPG

Salts	Impact sensitivity (<i>h</i> ₅₀ , cm)	Friction sensitivity (%)	Flame sensitivity (<i>h</i> ₅₀ , cm)
K(H ₂ TNPG)·H ₂ O	14.30	88	29.21
K ₂ (HTNPG)·H ₂ O	22.11	26	34.56
K ₃ (TNPG)·2(H ₂ O)	34.02	12	42.87

- [3] V.Y. Egorshv, V.P. Sinditskii, V.L. Zbarsky, Z.C. Yang, W.F. Liu, Synthesis and combustion study of metallic salts of trinitrophenol, in: *Theory and Practice of Energetic Materials. Parts A and B*, vol. 5, Science Press, Beijing/New York, 2004, pp. 30–37.
- [4] A.J. Bellamy, S.J. Ward, P. Golding, A new synthetic route to 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), *Propellants Explos. Pyrotech.* 27 (2002) 49–58.
- [5] A.J. Bellamy, S.J. Ward, P. Golding, Synthesis of ammonium diaminopicrate (ADAP), a new secondary explosive, *Propellants Explosives Pyrotech.* 27 (2002) 59–61.
- [6] J.C. Oxley, J.L. Smith, H. Ye, Thermal stability studies on a homologous series of nitroarenes, *J. Phys. Chem.* 99 (1995) 9593–9602.
- [7] C.S. Gyeong, N.K. Tai, G.E. Mee, Optimization of neural networks architecture for impact sensitivity of energetic molecules, *Bull. Korean Chem. Soc.* 26 (2005) 399–408.
- [8] T.B. Brill, T.L. Zhang, B.C. Tappan, Thermal decomposition of energetic materials 74. Volatile metal isocyanates from flash pyrolysis metal-NTO and metal-picrate salts and an application hypothesis, *Combust. Flame* 121 (2000) 662–670.
- [9] T.L. Zhang, R.Z. Hu, Y.J. Liang, F.P. Li, The preparation and thermal decomposition mechanism of alkali metal (Li, Na and K) salts of 3-nitro-1,2,4-triazol-5-one, *J. Therm. Anal.* 39 (1993) 662–667.
- [10] J.R. Song, Z.X. Chen, H.M. Xiao, R.Z. Hu, F.P. Li, K.B. Yu, Preparation, crystal structure and quantum chemical investigation of $[K(NTO)(H_2O)]$, *Acta Chim. Sinica* 56 (1998) 270–277.
- [11] D.E.G. Jones, P.D. Lightfoot, R.C. Fouchard, Q. Kwok, A.M. Turcotte, W. Ridley, Hazard characterization of KDNBF using a variety of different techniques, *Thermochim. Acta* 384 (2002) 57–69.
- [12] Mehilal, A.K. Sikder, S. Pawar, N. Skider, Synthesis, characterization, thermal and explosive properties of 4,6-dinitrobenzofuroxan salts, *J. Hazard. Mater.* 90 (2002) 221–227.
- [13] B. Shao, T.L. Zhang, J.G. Zhang, K.B. Yu, Crystal structure and molecular structure of $[C_6H_2(NO_2)_3K]_n$, *Chin. J. Energ. Mater.* 9 (2001) 122–125.
- [14] Y.F. Li, T.L. Zhang, J.G. Zhang, G.X. Ma, J.C. Song, K.B. Yu, Crystal structure and thermal decomposition mechanism of $[K(HTNR)(H_2O)]$, *Acta Chim. Sinica* 61 (2003) 1020–1024.
- [15] Y.F. Li, T.L. Zhang, J.G. Zhang, J.C. Song, G.X. Ma, Y.H. Sun, Preparation, molecular structure and thermal decomposition mechanism of $[K_2(TNR)(H_2O)]_n$, *Chin. J. Inorg. Chem.* 19 (2003) 861–864.
- [16] G.X. Ma, T.L. Zhang, J.G. Zhang, B. Shao, Y.F. Li, J.C. Song, K.B. Yu, Crystal structure and thermal decomposition mechanism of $[K(DNP)(H_2O)_{0.5}]_n$, *Chin. J. Chem.* 22 (2004) 131–135.
- [17] H.Y. Chen, T.L. Zhang, J.G. Zhang, X.J. Qiao, K.B. Yu, Crystal structure, thermal decomposition mechanism and explosive properties of $[Na(H_2TNP)(H_2O)_2]_n$, *J. Hazard. Mater.* 129 (2006) 31–36.
- [18] H.Y. Chen, T.L. Zhang, J.G. Zhang, K.B. Yu, The preparation, structures and thermal decomposition mechanisms of trinitrophenol hydrate, *Initiators Pyrotech.* 3 (2003) 34–38.
- [19] Z.T. Liu, Y.L. Lao, *Initiating Explosive Experimental*, Beijing Institute of Technology, China, 1995.
- [20] D.E.G. Jones, H.T. Feng, R.C. Fouchard, Kinetic studies of the thermal decomposition of KDNBF, a primer for explosives, *J. Therm. Anal. Calorim.* 60 (2000) 917–926.
- [21] Y.F. Li, *Research on Preparation, Properties and Applications of DNBF Series Compounds [D]*, Beijing Institute of Technology, 2004.