Full Paper

Vapor Pressure of Linear Nitrate Esters Determined by Transpiration Method in Combination with VO-GC/MS

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Abstract: Gas phase detection of explosives is an ongoing trend in the detection sciences. The conception of gas phase detection devices requires knowledge about gas phase concentration of the target analytes. Nitrate esters are well performing explosives with a high potential for misuse in improvised explosive devices that need to be detected at vulnerable infrastructures. With respect to this the six nitrate esters, ethyl nitrate (1), ethylene glycol dinitrate (2), glycerol trinitrate (3), meso-erythritol tetranitrate (4), D-mannitol hexanitrate (5) and pentaerythritol tetranitrate (6) were investigated in terms of detectability by vacuum out-let-GC/MS as potential components in improvised explosive devices. All compounds besides **5** could be detected using vacuum outlet GC/MS and their limits of detection were determined according to DIN 32645 : 2008. The vapor pressure of **2**–**4** was measured using the transpiration method. It was observed that the introduction of a $CHONO_2$ unit lowers the vapor pressure of the nitrate esters by about two orders of magnitude. For compound **4** the saturation concentration (73 $ng\,L^{-1}$) was compared with a vapor pressure based estimation of its concentration in diffusion equilibrium (0.385 $pg\,L^{-1}$).

1 Introduction

Nitrato compounds are the product of the esterificiation of (poly)-alcohols with nitric acid. Many molecules bearing this explosophore have been discovered in the 19th century. Figure 1 gives an overview of important representatives of this compound class with the year of first publication in scientific literature. Amongst these six representatives glyceryl trinitrate (GTN, **3**), more commonly known as nitroglycerine, is the compound that was published first in 1846 by *Sobrero* [1]. GTN (**3**) has been tamed by *Alfred Nobel* in 1866 by phlegmatization with Kieselgur as dynamite. Already *Sobrero* [1] knew about the tremendous toxicity of glyceryl trinitrate. The toxicity is caused by the vasodilative effect of nitrato compounds, which has been used in the pharmaceutical industry for the treatment of *Angina pectoris* [2]. Nitrato explosives still are widely distributed. Glyceryl trinitrate is used for mining explosives and double base propellants. Pentaerythritol tetranitrate (PETN **6**) is still in use as a booster explosive being appreciated for its readiness for detonation and high detonation pressure. Since the (poly-)alcohol starting materials for **1**–**5** are openly available to the public nitrato explosives are popular in the amateur chemist and terrorist scene. During the last years the increasing popularity and availability of the sweetening agents *meso*-erythritol and *D*-mannitol boosted the misuse of these food additives as an explosive precursor. With respect to this *Oxley at al.* [3–4] and *Matyas et al.* [5] investigated the analytical and energetic material properties of *meso*-erythritol tetranitrate (ETN, **4**). *Manner et al.* [6] published a crystallographic study of **4** in 2014. Within this work, being part of a project for gas phase detection of explosives [7], the gas phase detectability of the six nitrate esters ethyl nitrate (EtONO_2, **1**), ethylene glycol dinitrate (EGDN, **2**), glyceryl trinitrate (GTN, **3**), *meso*-erythritol tetranitrate (ETN, **4**), D-mannitol hexanitrate (MHN, **5**) and pentaerythritol tetranitrate (PETN, **6**) was investigated in terms of limits of detection and quantification using an improved method for vacuum outlet GC/MS (VO-GC/MS) [8] and vapor pressure measurements by the transpiration method [9–11] for compounds **2**–**4** to provide reliable data considering the ongoing trend of gas phase explosive detection [12–18]. This work is the first experimental application of VO-GC/MS using the advantages of placing the necessary restriction inside the GC-injector using an improved setup with a *Siltite®* μ-union column connector. Compounds **1**–**5** are of special interest in the detection sciences since their potential precursors are available to the public in many countries including Germany. Therefore compounds **1**–**5** are potential candidates for the use in improvised explosive devices and their risk potential will be evaluated in this work in terms of energetic performance using the EXPLO5 computer code and their sensitivity toward impact, friction and electrostatic discharge. For each material a convenient

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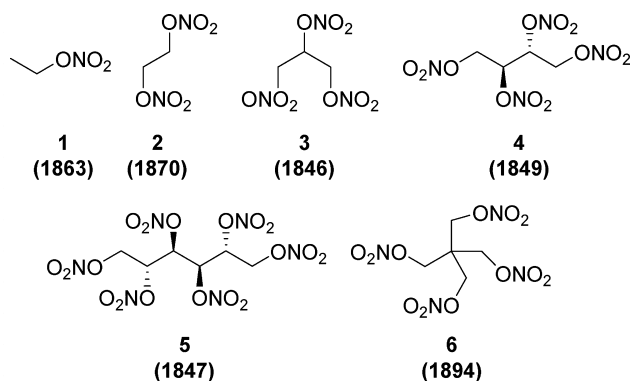**e-mail: tmk@cup.uni-muenchen.de*

Figure 1. Chemical Structures of ethyl nitrate (EtONO$_2$, **1**), ethylene glycol dinitrate (EGDN, **2**), glyceryl trinitrate (GTN, **3**), meso-erythritol tetranitate (ETN, **4**), D-mannitol hexanitrate (MHN, **5**) and pentaerythritol tetranitrate (PETN, **6**) with the year of first publication given in brackets.

method for small-scale synthesis resulting in high purity based on literature methods will be provided to facilitate the synthesis of reference materials for detection, training and instrument test purposes.

2 Experimental Section

2.1 Safety Aspects

The nitrate esters **1**–**6** are energetic materials with sensitivity to various stimuli. While we encountered no issues in the handling of these materials, proper protective measures (face shield, ear protection, body armor, Kevlar gloves and earthened equipment) should be used during the handling of explosive compounds including vapor pressure measurements.

2.2 Synthesis and Characterization of Explosives

This work provides safe and reproducible procedures for the small scale synthesis of nitrate esters **1**–**6**. (see ESI pp. S-2–S-6) The syntheses of nitrato compounds **1**–**6** from their corresponding (poly-)alcohol starting materials were adapted from literature procedures which are stated in the experimental section. For safety reasons the purity of compounds **1**–**3** was assessed by ^{1}H NMR spectroscopy and VO-GC/MS. No impurities could be identified in compounds EtONO$_2$ **1** and EGDN **2**. The VO-GC/MS chromatogram of GTN **3** revealed a 1% impurity of glyceryl dinitrate based on signal area integration. The synthesis of ETN **4** and MHN **5** is carried out according to literature procedures with slight modifications. The protocol for the synthesis of PETN **6** was developed in our workgroup using *in situ* generated acetyl nitrate since initial attempts based on literature procedures were not satisfying in terms of product purity.

Within this work the crystal structure of MHN **5** at 100 K was elucidated for the first time and remeasurements of the crystal structure of ETN **4** at 100 K and 291 K were carried out. (see ESI pp. S-7–S-9) For all compounds **1**–**6** the friction and impact sensitivities were determined according to STANAG 4489 [19] and 4487 [20] with modified instructions [21–22] using a BAM impact and friction tester [23–24]. The sensitivity toward electrostatic discharge was determined using a testing device by OZM [25]. Melting and decomposition temperatures were determined with an OZM DTA device or a Linseis differential scanning calorimeter with a heating rate of 5 °C min^{-1}. The heat of formation of all analytes was calculated with Gaussian 09 [26] on a CBS-4 M level. The room temperature densities of **4**–**6** were determined using a Quantachrome Ultrapyc 1200e gas pycnometer. Based on room temperature density and heat of formation the energetic performance of the explosives was calculated using the EXPLO5v6.03 computer code.

2.3 Vacuum Outlet GC/MS for Detection of Nitrate Esters

The gas-chromatography (GC) analysis of thermolabile analytes, which can be low-volatile, like nitrate esters, is a delicate task since this analytical technique requires the transfer of the analyte into the gaseous state at elevated temperatures of operation in the typical range of 30 to 300 °C. The decomposition temperature of the analyte should be avoided throughout the analysis and its residence time in hotter zones like the injector minimized. The analytical GC column should be short enough to allow elution of the analyte without decomposition. In general two approaches for this problem exist. In case of atmospheric pressure detectors like the electron capture detector (ECD) the elution temperatures and retention times of the analytes can be reduced by increased carrier gas flow rates [27]. The beneficial use of analyte protectants for the GC/MS and GC/ECD-analysis of explosives has been demonstrated by *Kirchner et al.* [28]. Recently *Boeker et al.* [29] presented the application of flow field thermal gradient gas chromatography as a new technique for the analysis of explosives. In this work vacuum outlet gas-liquid-chromatography as established by *de Zeeuw et al.* [8] was chosen for the evaluation of the methods potential for the detection and quantification of nitrate esters **1**–**6**. The method uses a restriction capillary which is positioned inside the GC injector to limit the flow of carrier gas into a wide-bore analytical column (*Restek®* RTX-TNT, 6 m, 0.53 mm i.d., 1.5 μm film thickness). Placing the restriction in front of the analytical column results in a gradual expansion of the detector vacuum along the analytical column and increased optimum carrier gas velocities, which lowers the analyte elution temperatures. In the original literature [8] *Restek®* press-tight glass connectors and *Uniliner* were used for the connection of restriction and analytical column. Since both solutions are not compatible with the *Shimadzu®* GCMS QP2010 SE in combination with an *Atas®*

Optic 4 injector used in this work a *SGE SilTite®* μ-union column connector with an outer diameter of 3.5 mm was used in combination with a custom-made stainless steel liner (5 mm outer diameter, 0.5 mm wall thickness, split notches at bottom end). The numerous advantages of placing the restriction inside the injector were elucidated by *de Zeeuw et al.* [8], but an important aspect was not mentioned: the GC-injector can be operated in constant pressure mode. Calculations that are based on the *Hagen-Poiseuille* equation [30] demonstrate that the flow-dynamics of the restriction-column assembly are dominated by the restriction in the isothermal injector and a change of the column oven temperature from 40 °C to 280 °C results in a negligible change of calculated column flow from 4.08 mL min^{-1} to 3.92 mL min^{-1} (see ESI p. S–10).

2.4 Transpiration Method Vapor Pressure Determination

For the transpiration experiment a carrier gas stream (nitrogen 5.0) is conducted over a P_4O_{10} drying tower to remove any traces of moisture before the gas flow rate is regulated with a mass flow controller (Natec Sensors MC-100 CCM) with flow rates from 1 to 5 L h^{-1}. The flow-regulated gas stream then passes the saturator, which is a U-shaped glass tube (50 cm length, 8 mm i.d.) embedded in a cylindrical glass vessel (height: 25 cm, diameter: 10 cm). (see ESI Figure S-7) The temperature of the saturator is controlled by a circulation thermostat. (Huber Ministat 230 with external class A PT-100 sensor pumping a thermofluid through the saturator) The analyte of choice is dispersed on 1 mm glass beads (Edmund Bühler GmbH #0001067) and filled into the saturator. As the carrier gas stream passes the saturator it reaches its saturation equilibrium with the analyte and is condensed in a cold trap at −30 °C. The vapor pressure of the analyte p_{sat} at the experimental temperature T_{exp} can be calculated according to the following equation based on the validity of the Ideal Gas Law and the Dalton's Law of partial pressures:

$$p_{sat}(T_{exp}) = \frac{m_a R T_{amb}}{M V_{amb}} \tag{1}$$

p_{sat}: vapor pressure of the analyte [Pa], T_{exp}: temperature of the saturator [K], m_a: mass of analyte [kg], T_{amb}: ambient temperature [K], V_{amb}: volume of carrier gas at ambient conditions [m^3], M: molecular weight of the analyte [kg mol^{-1}], R: universal gas constant: 8.314469 J mol^{-1} K^{-1}

The volume of the carrier gas V_{amb} is measured at ambient conditions by measuring its flowrate with a soap film flowmeter at the ambient temperature T_{amb} with the assumption that the volume of carrier gas is significantly higher than the volume of the gaseous analyte. The mass of the analyte m_a is determined by VO-GC/MS quantification using *n*-alkanes (C-12, C-14 or C-16) as an internal standard,

which is added to the trap as acetone solution of known concentration.

The p_{sat}-T_{exp} values obtained for each analyte are analyzed with a fitting function:

$$\ln \frac{p_{sat}}{p^\circ} - \frac{\Delta_{l/cr}^g C_{p,m}^\circ}{R} \ln \frac{T}{T_0} = A - \frac{B}{T} \tag{2}$$

p°: reference pressure (1 Pa), $\Delta_{l/cr}^g C_{p,m}^\circ$: difference between the heat capacity of the liquid (l, for vaporization) or crystalline (cr, for sublimation) and the gaseous state [J mol^{-1} K^{-1}], T: temperature [K], T_0: reference temperature [K], A / B: fitting coefficients (A: [ ], B: [K]).

The enthalpy of vaporization or sublimation at the temperature T can be calculated by:

$$\Delta_{l/cr}^g H_m^\circ(T) = RB + \Delta_{l/cr}^g C_{p,m}^\circ T \tag{3}$$

$\Delta_{l/cr}^g H_m^\circ(T)$: molar enthalpy of vaporization (l) or sublimation (cr).

The heat capacities $C_{p,m}^\circ$ of the analytes **2**–**4** in liquid or crystalline state are either available in the literature or calculated according to the empirical element-increment approach by *Hurst et al.* [31]. (see ESI Table S-3) The corresponding heat capacity differences with the gaseous state are calculated according to the procedures by *Chickos et al.* [32].

3 Results and Discussion

3.1 Energetic Performance and Sensitivities

Table S-2 compiles the energetic performance and sensitivity parameters of nitrate esters **1**–**6**. The sensitivity classification in the following is carried out according to the UN Recommendations on the Transport of Dangerous Goods [33]. Compounds **1**–**3** are liquids at room temperature and insensitive toward friction (> 360 N), yet very sensitive toward impact (1 J). The sensitivity toward electrostatic discharge cannot be measured for liquids with the used testing device. ETN (**4**), MHN (**5**) and PETN (**6**) are solids, which are very sensitive toward impact (3 J for **4** and **6**) and friction (60 N for **4** and **6**). MHN **5** is more sensitive toward impact (1 J) and friction (30 N) than ETN (**4**) and PETN (**6**). Compounds **2**–**6** have positive or equilibrated oxygen balances Ω_{CO2} [34]. The exothermic heats of formation were calculated on a CBS-4M level using Gaussian 09 [26]. The discrepancies between experimental and calculated enthalpy of formation are in the range of the accuracy of the CBS-4M method. For the reason of comparability the calculated values were used for the calculation of the energetic performance parameters. All nitrato compounds **1**–**6** are classical explosives that derive their energetic performance from the oxidation of their carbon backbone. The energetic performance parameters were calculated with the EXPLO5

(v6.03) computer code at the room temperature theoretical maximum density. Due to the low density **1** is the worst performing explosive. Compounds **2**–**5** are closely related in terms of their molecular structure since they only differ in the number of methylene nitrato (CH_2ONO_2) units. The introduction of these units increases the density of the molecule. According to the *Kamlet-Jacobs* equations [35] the detonation velocity is directly proportional to the density and the detonation pressure is proportional to the squared density. Compounds **4** (V_{det} 8540 m s^{-1}; p_{C-J} 301 kbar) and **5** (V_{det} 8490 m s^{-1}; p_{C-J} 296 kbar) outperform PETN **6** (V_{det} 7655 m s^{-1}; p_{C-J} 298 kbar) in terms of detonation velocity with equal (**4**) or higher (**5**) sensitivity towards external stimuli, which is owed to the thermally stabilizing quarternary carbon unit in **6**. With respect to the high energetic performance and availability of the corresponding polyol starting materials **4** and **5** should be considered a seriously dangerous in the context of improvised explosive devices. All nitrate esters **1**–**6** melt prior to decomposition with increasing melting and decomposition temperatures from **1** to **6**.

3.2 Thermolability of ETN 4

A sample of **4** which was repeatedly molten and resolidified did not show any significant signs of decomposition in the ^{1}H NMR spectrum. For the vapor pressure measurement of **4** the compound was subjected to temperatures ranging from 25 to 65 °C over a period of two weeks. This led to first products of decomposition (see ESI Figure S-8). Therefore ETN **4** should not be considered a high performance meltcast explosive with long-term stability. Due to the close structural relation MHN **5** might show the same behavior. Long-term decomposition was not observed when compounds **1**–**5** were stored in an argon atmosphere at −30 °C.
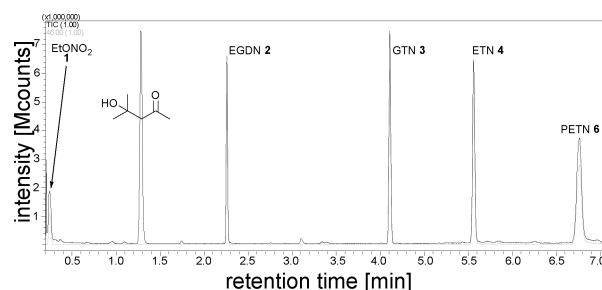

Figure 2. Vacuum Outlet GC/MS-Chromatogramm of a mixture containing nitrate esters **1**–**6** in acetone. Analyte concentration: 0.46 µmol mL^{-1} Black: Total Ion Count (TIC) chromatogram, grey: chromatogram of m/z 46 amu.

3.3 VO-GC/MS

The VO-GC/MS setup and method in this work allows the successful detection and detection of nitrate esters **1**–**4** and PETN **6**, which is demonstrated by the measurement of a mixture of nitrate esters **1**–**6** in acetone. (see Figure 2, Table 1). MHN **5** could not be detected using the VO-GC/MS setup, which is presumably caused by decreased volatility in comparison to the other analytes. The exact GC/MS measurement parameters used in this work can be found in ESI Table S-4.

Table 1 is a compilation of GC/MS retention times and elution temperatures, NIST match scores and relative intensities of the selected fragment ions m/z 30, 46 and 76 amu. These mass fragments are the most intense peaks in the VO-GC/MS spectra of **2**, **3**, **4** and **6**. (see ESI p. S-16) Due to the high N,O content of the compounds the fragment ions m/z 30, 46 and 76 correspond potentially to the nitrosonium cation (NO$^+$, 29.9974 amu), nitronium cation (NO$_2^+$, 45.9924 amu) and the N$_2$O$_3^+$ cation (75.9903 amu). These predominant fragments are useful for the development of selective ion monitoring methods. The NIST match scores are in the range from 76 % for PETN **6** to 96 % for EGDN **2**. In general the agreement of relative intensities of the fragment ions for VO-GC/MS, direct electron ionization

Table 1. GC/MS retention times and elution temperatures, NIST match scores and relative intensities of mass fragments $m/z = 30$, 46 and 76.

cpd.[a]	t_{ret}[b] [min]	$T_{elution}$[c] [°C]	NIST[d] [%]	m/z 30[e] [%]	m/z 46[e] [%]	m/z 76[e] [%]	R^2[f]	LOD/LOQ[g] [pg]
1	0.24	30.0	88	17/9.5/12.8	100/100/100	17.5/38.5/35.2	0.9999	3/11
2	2.26	80.4	96	15.0/9.5/22.0	100/100/100	6.2/14.5/11.2	0.9999	24/85
3	4.11	121.5	94	4.4/82.9/16.4	100/100/100	12.2/99.1/55.2	0.9999	42/148
4	5.06	150.0	n.a.	13.3/12.1/n.a.	100/100/n.a.	3.0/8.2/n.a.	0.9938	424/1839
5	n.m.	n.m	n.m.	n.m/20.3/n.a.	n.m./100/n.a.	n.m./6.3/n.a.	n.m.	n.m.
6	6.27	150.0	76	9.7/7.6/0	100/100/88.4	8.6/19.9/100	0.9991	123/429

a) Number of compound according to Figure 1 b) retention time of compound in VO-GC/MS analysis c) Elution temperature in VO-GC/MS analysis d) NIST 08 Library search match score after background subtraction e) Relative spectral intensity of corresponding mass channel (VO-GC/MS / DEI-MS/NIST 08). (DEI: direct electron ionization) f) R^2 of linear calibration for full range calibration g) Limit of Detection/Limit of Quantification according to DIN 32645:2008 with $\alpha = °\beta = 0.01$ and k = 3. n.m.: not measured, n.a.: not available.

(DEI) MS and the NIST 08 library is poor for all compounds. It should be preferred to establish an internal mass spectra database for each instrument. The limits of detection (LOD) and quantification (LOQ) were calculated according to DIN 32645:2008. Both parameters increase with the molecular weight of the analyte. The LOD and LOQ of **6** are lower than that of **4**. This is presumably caused by the better thermostability of **6**. The details of calculation can be found in ESI pp. S-17–S-18.

3.4 Vapor Pressure Measurements

The detection of hazardous materials like explosives in the gaseous phase is a relatively new trend in the development of detection instruments [12–18]. The knowledge of the vapor concentration of the analyte is essential for the definition of the air volume that needs to be sampled for exceeding the limit of detection of the applied detector system. The vapor pressure is the physico-chemical parameter that is linked to the saturation equilibrium concentration of the analytes to be detected. We recently published our results with the transpiration method for amitone and its derivatives (including 5 reference compounds) [48], for the peroxide explosives TATP and DADP [49], mononitrotoluenes [50] and aliphatic nitroalkanes [51]. With the experience gained in these projects we decided to apply the transpiration method for the measurement of the vapor pressure of nitrate esters EGDN **2**, GTN **3** and ETN **4**. Therefore the vapor pressure at ambient temperatures of **2** (274–318 K), **3** (283–328 K) and **4** (298–338 K) was measured in this work with the transpiration method [9–11] and compared critically with the literature data available to establish vapor pressure and enthalpy of vaporization $\Delta_l^g H_m^\circ$ at the reference temperature 298.15 K for **2** and **3** and sublimation $\Delta_{cr}^g H_m^\circ$ (298.15 K) for the room temperature solid ETN **4**. The transpiration method is a well-established [9–11] method method for the determination of vapor pressures for medium to low volatility analytes and therefore suitable for analytes **2**–**4**.

Experimental absolute vapor pressures measured by the transpiration method, coefficients *A* and *B* of Eq. (2), and vaporization enthalpies of analytes **2**–**4** derived from Eq. (3) are given in ESI pp. S-19–S-24. The procedure for calculation of the combined uncertainties of the vaporization enthalpy was described elsewhere [9]. They include uncertainties from the transpiration experimental conditions, uncertainties of vapor pressure and uncertainties from temperature adjustment to $T = 298.15$ K. We also collected available experimental literature data on vapor pressures of analytes **2**–**4**. Actually, authors not always derived vaporization enthalpies from their vapor pressures or performed it in different manner. We treated the literature vapor pressures using Eqs. (2) and (3) and calculated enthalpies of vaporization or sublimation at (298.15 K) for the sake of comparison with our results. Table 2 is a compilation of the

results obtained in this work in comparison with literature values concerning the vaporization and sublimation enthalpies investigated at the average temperature of the measurement and the reference temperature 298.15 K. Additionally the vapor pressure at 298.15 K is stated. The absolute vapor pressures p_{sat} and thermodynamic properties of vaporization or sublimation obtained by the transpiration method in this work and *Clausius-Clapeyron* plots of own and literature data are available for all analytes in ESI pp. S-19–S-24.

The vaporization behavior of the analytes **2**–**4** was studied in this work in the temperature range from 274.1–318.2 K for **2**, 283.2–328.0 K for **3** and 338.0–367.8 K for **4**. The enthalpies of vaporization derived from the data obtained in this work and adjusted to 298.15 K are: 65.1 ± 0.3 kJ mol^{-1} for **2**, 86.7 ± 0.4 kJ mol^{-1} for **3** and 101.6 ± 1.1 kJ mol^{-1} for **4**. For compound **4** an enthalpy of sublimation at 298.15 K of 129.1 ± 1.1 kJ mol^{-1} was derived from the measurements. The vapor pressures at 298.15 K derived from the p-T-data obtained in this work are: 12.1 Pa for **2**, 82.2 mPa for **3** and 0.6 mPa for **4**. A Clausius-Clapeyron-plot of the data obtained in this work for compounds **2**–**4** is provided in Figure 3.

For EGDN **2**, available p-T literature data for comparison are three transpiration experiments by *Pella et al.* [36–37], *Brandner et al.* [39] and *Crater et al.* [40], an isotope dilution experiment by *St. John et al.* [38] and an air bubbling measurement by *Rinkenbach et al.* [41]. The isotope dilution data stated by *St. John et al.* [38] is considered erroneous in comparison with the other p-T-datasets available (cf. ESI Fig-
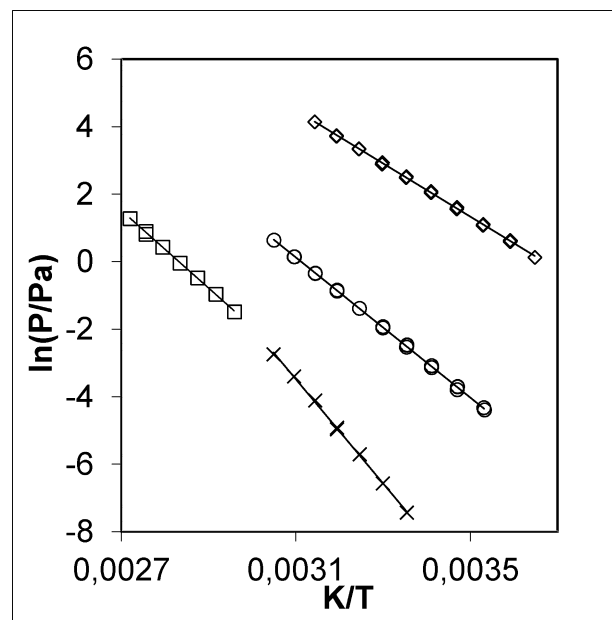

Figure 3. Clausius-Clapeyron (ln p vs 1/T) plot of the p-T-data obtained in this work for the vaporization of **2** (◇), GTN **3** (○),**4** (□) and the sublimation of **4** (×).

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Table 2. Compilation of data on available on enthalpies of vaporization $\Delta_l^g H_m^\circ$ of **2**, **3** and **4**, enthalpy of sublimation $\Delta_{cr}^g H_m^\circ$ of **4** and vapor pressures of compounds **1–4** *at 298.15 K.*

Experiment[a]	M[b]	T-Range K	T_{avg} K	$\Delta_l^g H_m^\circ(T_{avg})$ kJ mol^{-1}	$\Delta_l^g H_m^\circ$(298.2 K)[c] kJ mol^{-1}	p_{sat}[d] mPa
2 (l) This Work	T	274.1–318.2	294.3	65.4 ± 0.3	65.1 ± 0.3	12.1 × 10³
Pella 1977 [36–37]	T	254.7–298.2	272.5	65.2 ± 0.1	63.7 ± 0.3	10 × 10³
St. John 1975 [38]	I	–	298.2	–	–	(3.7 × 10³)
Brandner 1938 [39]	T	283.2–323.2	302.6	68.0 ± 0.2	68.3 ± 0.3	10.6 × 10³
Crater 1929 [40]	T	288.2–328.2	307.5	72.8 ± 1.7	73.4 ± 1.7	9.5 × 10³
Rinkenbach 1926 [41]	A	273.2–295.2	283.7	63.6	(62.9)	9.8 × 10³
Average EGDN 2 (l)					65.8 ± 0.2[e]	10.4 × 10³[f]
3 (l) This Work	T	283.2–328.0	302.8	86.1 ± 0.4	86.7 ± 0.4	82.2
Tunnell 2015 [42]	T	290.2–308.6	299.9	70.2 ± 4.8	(70.3 ± 4.9)	(47.8)
Mirosh. 1988 [43]	C	–	298.2	92.0 ± 2.1	92.0 ± 2.1	
Dionne 1986 [44]	T	–	299.2	–	–	(41.4)
St. John 1975 [38]	I	–	298.2	–	–	(3.2)
Dravnicks 1972 [45]	T	–	298.2	–	–	66.7
Kemp 1957 [46]	T	293.2–313.2	303.5	107.3 ± 2.9	107.8 ± 2.9	58.7
Brandner 1938 [39]	T	283.2–323.2	302.6	80.3 ± 0.4	80.7 ± 0.5	88.4
Marshall 1916 [47]	T	293.2–366.6	332.2	85.9 ± 0.4	89.1 ± 0.5	60.4
Average GTN 3 (l)					86.0 ± 0.3[e]	71.3[f]
4 (l) This Work	T	338.0–367.8	353.9	95.1 ± 0.9[g]	101.6 ± 1.0[g]	
Experiment[a]	M[b]	T-Range	T_{avg}	$\Delta_{cr}^g H_m^\circ(T_{avg})$	$\Delta_{cr}^g H_m^\circ$(298.2 K)[c]	p_{sat}[d]
4 (cr) This Work	T	298.2–331.0	316.5	131.8 ± 1.1[g]	129.1 ± 1.1[g]	0.6[g]
Oxley 2012 [3–4]	G,O	316.2–331.2	323.7	117.7	119	3.2

a) First author and year of publication b) Methods: T: Transpiration, I: Isotope Dilution, A: Air Bubbling, G: Thermogravimetry, O: Equation Only c) Enthalpies of vaporization or sublimation were adjusted according to *Chickos et al.* [31] with the heat capacity parameters stated in Table S-3 d) Vapor pressure at 298.15 K, calculated according to equation (2) from the individual fitting parameters of each dataset e) Weighted average value, calculated using the uncertainty as the weighing factor f) Average value. Values in brackets were excluded from average value calculation g) Value has to be regarded critically due to unavoidable slow decomposition of ETN **4**.

ure S-9) and is therefore disregarded. Isotope dilution measurements are not a well-established method of choice for vapor pressure measurements and may suffer from various error sources including isotope effects. *Rinkenbach et al.* [41] published solely two datapoints. This is insufficient for an error estimation – the data was therefore excluded from average value calculation.

For GTN **3**, available p-T literature data for comparison are seven transpiration experiments by *Brandner et al.* [39], *Tunnell et al.* [42], *Dionne et al.* [44], *Dravnicks et al.* [45], *Kemp et al.* [46] and *Marshall et al.* [47] and one isotope dilution measurement by *St. John et al.* [38]. The isotope dilution data stated by *John et al.* [38] is disregarded for the reasons stated above. (cf. ESI Figure S-10) The enthalpy of vaporization at 298.15 K derived from the p-T-data of the

most recent transpiration data reported by *Tunnell et al.* [42] is the lowest and most imprecise value available (cf. Table 2, $70.3 \pm 4.9 \text{ kJ mol}^{-1}$). With respect to this their experiment is neglected in the calculation of recommended values. *Miroshnichenko et al.* [43] report calorimetric data for the enthalpy of vaporization of nitroglycerine at 298.15 K. Their value is higher than the one derived in this work. This might be caused by a dinitroglycerol sample impurity of 0.2 or 1.2 mass % stated by the authors. The enthalpy of vaporization at 298.15 K was derived from measurements in the temperature range from 40–120 °C, yet no statement about the sample purity after the measurements at relatively high temperatures was given. Considering this the value stated by *Miroshnichenko et al.* [43] should be regarded critically.

The sublimation behavior of the room temperature solid ETN **4** was studied in the temperature range of 298.2–331.0 K. The vapor pressure of ETN **4** at 298.15 K has been estimated via isothermal gravimetry by *Oxley et al.* [3–4]. This work is the first characterization of the sublimation and vaporization of ETN **4** with the well-established transpiration method, yet the values have to be considered estimates due to the unavoidable slow decomposition of the analyte, which was elucidated before. (cf. ESI Figure S-8). The literature data provided by *Oxley et al.* [3–4] for ETN **4** is an Antoine equation in the temperature range of 43 °C to 58 °C and a vapor pressure at 298.15 K that was obtained by extrapolation in the original work. The values obtained in this work ($101.6 \pm 1.0 \text{ kJ mol}^{-1}$, 0.6 mPa) are not in agreement with the values published by *Oxley et al.* [3–4] ($119.0 \text{ kJ mol}^{-1}$, 3.2 mPa), which are influenced presumably by the same decomposition problem observed in this work. Furthermore the pressure analog values obtained by thermogravimetric measurements were converted into vapor pressure values by reference material calibration with benzoic acid which is a suitable approximation for estimates but also an additional potential source of systematic error considering the absolute vapor pressures.

Oxley et al. [3–4] state an enthalpy of fusion for ETN **4** obtained by differential scanning calorimetry at heating rates from 1 to 20 K min^{-1}. The values spread from 29.9 kJ mol^{-1} to 35.3 kJ mol^{-1} at endotherm temperatures from 59 to 63 °C. After adjusting the values to 298.15 K according to *Chickos et al.* [32] using the heat capacity differences in ESI Table S-3 the values spread from 27.4 kJ mol^{-1} to 32.9 kJ mol^{-1} which results in an average value of $30.2 \pm 2.8 \text{ kJ mol}^{-1}$ for the enthalpy of fusion at 298.15 K.

Considering the relationship of the enthalpies of vaporization, sublimation and fusion at 298.15 K [32]:

$$\Delta_l^g H_m^\circ = \Delta_{cr}^g H_m^\circ - \Delta_{cr}^l H_m^\circ \quad (4)$$

The enthalpy of vaporization can be derived from the enthalpy of sublimation obtained in this work: $\Delta_l^g H_m^\circ = 129.1 \text{ kJ} \pm 1.1 \text{ kJ mol}^{-1} - 30.2 \pm 2.8 \text{ kJ mol}^{-1} = 98.9 \pm 3.0 \text{ kJ mol}^{-1}$.

This approximated value is in fair agreement with the value for the enthalpy of vaporization at 298.15 K of $101.6 \pm 1.0 \text{ kJ mol}^{-1}$ measured in this work and proves the internal consistency of the data obtained despite the decomposition problem. For this reason the data published by *Oxley et al.* [3–4] should be regarded critically since their enthalpy of sublimation seems too low. The vapor pressure at 298.15 K (0.6 mPa) estimated in this work is in rough agreement with that derived from the data by *Oxley et al.* (3.2 mPa) [3–4].

Based on the literature data available uncertainty weighted average values for the enthalpies of vaporization at 298.15 K and average values for the vapor pressure at 298.15 were calculated for **2** ($65.8 \pm 0.2 \text{ kJ mol}^{-1}$, 10.4 Pa) and **3** ($86.0 \pm 0.3 \text{ kJ mol}^{-1}$, 71.3 mPa). These values are in fair agreement with the data obtained in this work. (**2**: $65.1 \pm 0.3 \text{ kJ mol}^{-1}$, 12.1 Pa; **3**: $86.7 \pm 0.4 \text{ kJ mol}^{-1}$, 82.2 mPa). Compounds **2**–**4** have similar structures but differ in the number of $CHONO_2$ units. With respect to the data recommended and obtained in this work the vapor pressure at 298.15 K is lowered by two orders of magnitude for each additional $CHONO_2$ unit. It is hard to measure the vapor pressure of **5**, yet it can be estimated that it should be lower than that of **4** (0.6 mPa at 298.15 K, measured in this work) by a factor of 10^4. This is a convenient explanation for its non-detectability by the VO-GC/MS method. Since **5** has the best energetic performance parameters (cf. Table S-2) but is the least volatile material with a high degree of precursor availability (as sweetening agent), it should be a benchmark analyte for the development of new explosive detection methods. Its sublimation behavior should be further investigated with low-temperature high precision methods like Knudsen-effusion and Quartz-crystal microbalances.

4 Conclusions

In this work the nitrate esters ethyl nitrate (EtONO$_2$, **1**), ethylene glycol dinitrate (EGDN, **2**), glyceryl trinitrate (GTN, **3**), *meso*-erythritol tetranitrate (ETN, **4**), D-mannitol hexanitrate (MHN, **5**) and pentaerythritol tetranitrate (PETN, **6**) were fully characterized in terms of classical chemical characterization, sensitivity toward external stimuli and energetic performance. It could be shown that compounds **1**–**5**, potential candidates in improvised explosive devices, are well-performing explosives with high sensitivity toward external stimuli. With respect to their gas-phase detectability the vapor pressure of compounds **2**–**4** was investigated. It could be demonstrated that the introduction of a $CHONO_2$ unit in linear nitrate esters lowers the vapor pressure by about two orders of magnitude. With respect to their vapor pressure p_{sat} at 298.2 K (**2**: 10.4 Pa, **3**: 0.071 Pa, **4**: 0.0032 Pa) the saturation concentration c_{sat} of the explosives can be calculated according to the ideal gas equation: $c_{sat} \text{ [mg L}^{-1}] = p_{sat} \times M/(R \times 298.15 \text{ K})$ The resulting values are: EGDN **2**: 742.2 µg L^{-1}, GTN **3**: 7.529 µg L^{-1} ETN **4**: $\approx 73 \text{ ng L}^{-1}$ and

PETN 6: 0.198 ng L^{-1}. These values have to be considered as the maximum concentration observable. Calculations based on a mathematical model published by *Dravnicks et al.* [45] based on Fick's Law of diffusion (see ESI 10, exposed explosive surface 200 cm^2, 298.15 K) result in a non-equilibrium concentration for ETN **4** of 0.386 pg L^{-1}, which is lowered by about a factor of 190,000 in comparison to the saturation concentration. The limit of detection of **4** is 424 pg on column. For PETN **6** the detection limit is 123 pg on column and the non-equilibrium concentration 0.977 fg L^{-1} (same conditions). In case of an application of VO-GC/MS for gas phase detection of nitrate esters an air sampling unit needs to be constructed which collects the analytes of interest by adsorption followed by thermal desorption and lossless transfer to the analytical column. This concept was realized in Project SEDET [18]. For ETN **4** 1.098 m^3 of air need to be sampled for exceeding the limit of detection. For PETN **6** an air sampling volume of 138 m^3 would be necessary. This indicates that the gas-phase detectability of an explosive is dictated by the vapor pressure of the compound and its corresponding limit of detection. Although this calculation is just an estimate it demonstrates the feasibility of gas-phase detection of explosives since five of six nitrate esters can be detected using VO-GC/MS. The remaining challenge is the construction of a sampling unit which allows the sampling of high volumes of air and subsequent transfer to the detector system with high efficiency.

Acknowledgements

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