

Experimental Vapor Pressures of Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and Hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX)

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Abstract: In this work experimental vapor pressures of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX) were measured with transpiration method. Corresponding enthalpies of sublimation were determined to be $(130.9 \pm 2.1) \text{ kJ mol}^{-1}$ and

$(108.1 \pm 1.6) \text{ kJ mol}^{-1}$, respectively. Along with the experimental data fitting equations are reported and p - T data extrapolated to 298.15 K to be $0.71 \mu\text{Pa}$ for RDX and $823 \mu\text{Pa}$ for TNX.

Keywords: Vapor Pressure · High explosives · Gas-saturation · Enthalpy of sublimation

1 Introduction

With the increase of reported terrorist attacks throughout last decades, there is a great scientific interest in the detection of potentially hazardous materials [1]. Vapor pressure is a vital parameter when it comes to gas-phase detection of such materials. Extensive efforts have been given throughout the years to determine vapor pressures of most common explosives. Two comprehensive reviews on vapor pressures have been published by Östmark *et al.* [2] and Ewing *et al.* [3]. These reviews emphasize on the need of experimental vapor pressures over a broad temperature range, also yielding other thermodynamic properties, such as enthalpy of sublimation/vaporization. Unfortunately, the reported vapor pressures of explosives often differ significantly. Since the release of these reviews, several studies have been published by our group with the aim of providing reliable experimental vapor pressure data on a variety of explosives [4].

One of the most commonly used high explosives hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) has great importance in military use: it is one of the main ingredients in most commonly used explosive mixture compositions [5]. It has relatively low sensitivity and high thermal stability. Regardless the wide use of this high explosive, obtaining experimental vapor pressures of RDX has been hindered by the fact that RDX possesses a very low vapor pressure. Several attempts have been made in the past, however, most of the results in various literature sources are inconsistent, as discussed below. For this reason, this work focused on the determination of reliable experimental vapor pressures of RDX in a temperature range from 342.4 to 397.1 K.

As a result of wide use of RDX in military applications, the degradation of the chemical has been studied extensively. It has been shown that under environmental con-

ditions nitro groups of RDX tend to transform into nitroso derivatives or cleave the N-NO₂ bonds producing labile products [6]. None of the decomposition products are known to occur naturally, therefore, the detection of them can indicate the current or past presence of RDX [7]. One of the nitroso derivatives hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX) could be a signature compound when detecting the presence of RDX in the environment. Moreover, this compound is known in the amateur chemist scene and in the past has been used in improvised explosive devices (IED) [8]. For these reasons, experimental vapor pressures in a temperature range from 312.6 to 357.1 K are reported in this work.

2 Experimental Section

2.1 Materials

Caution! RDX and TNX are toxic and should be handled with caution! Proper protective measures (gloves, safety

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goggles, laboratory coats, etc.) should always be used during handling of the compounds.

RDX was synthesized according to the procedure described in the thesis of Steeman [9]. TNX was prepared according to the procedure described in the work of Rothstein *et al.* [10]. The purity of the compounds used in this study (Figure 1) was tested by EA, ^1H -, ^{13}C -, ^{14}N -NMR, and HPLC-DAD techniques. Purity data are disclosed in the Table 1. For further details see Supporting Information.

2.2 Transpiration Method

The vapor pressure of the compounds was measured using the transpiration method, which was described in detail before [11]. Between 0.5 and 1 g of analyte was used to coat 1 mm diameter glass beads. In the case of RDX, the compound was dissolved in acetone and added to the glass beads. The resulting suspension was dried in a rotational evaporator until the solvent is completely evaporated and then transferred into a thermostatted glass saturator. In case of TNX, compound was carefully layered with beads directly into the saturator. A dry nitrogen stream was passed through the temperature-controlled saturator and the transported analyte was collected in a glass tube, immersed in a cooling trap. The amount of collected analyte was determined by HPLC-DAD analysis using a suitable internal standard. Further information about the methods used is provided in the Supporting Information. The validity of the experimental setup in conjunction with the HPLC-DAD instrument was tested previously with several reference materials of well-established vapor pressures (naphthalene, anthracene, etc.) [11a].

The calculation of vapor pressure p_{sat} at the temperature of saturator T_{exp} relies on Dalton's law of partial pressures

(under assumption that the volume of the analyte in the gas phase is negligible) and the Ideal Gas Law:

$$p_{\text{sat}}(T_{\text{exp}}) = \frac{m_a RT_{\text{amb}}}{MV_{\text{amb}}} \quad (1)$$

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

Resulting experimental p - T values are fitted according to equation 2:

$$\ln\left(\frac{p_{\text{sat}}}{p^\circ}\right) - \frac{\Delta_{\text{cr}}^g C_{p,m}^\circ}{R} \ln \frac{T}{T_0} = A - \frac{B}{T} \quad (2)$$

p° : reference pressure (1 Pa), $\Delta_{\text{cr}}^g C_{p,m}^\circ$: molar heat capacity difference between crystalline (cr) and gaseous phase (g) at constant pressure [$\text{J mol}^{-1} \text{ K}^{-1}$], T : temperature [K], T_0 : reference temperature [K], A/B : fitting coefficients (A : unitless coefficient [], B : [K]).

Calculation of molar enthalpy of sublimation $\Delta_{\text{cr}}^g H_m^\circ$ at temperature T was performed using the equation 3:

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

This approach was used to analyse both own and literature data.

The molar heat capacity at constant pressure $C_{p,m}^\circ$ for RDX was available in the literature [12]. The value for TNX was obtained with the empirical increment approach by Hurst *et al.* [13]. Molar heat capacity differences were obtained by a procedure described by Chickos *et al.* [14]. The values are detailed in Table 2.

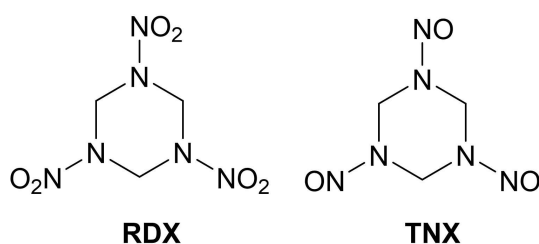


Figure 1. Compounds studied in this work: hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX).

Table 1. Purity of the compounds investigated.

Substance	CAS#	Purity ^a
RDX	121-82-4	0.999
TNX	13980-04-6	0.999

^a Mass fraction purity was determined by HPLC-DAD.

Table 2. Molar heat capacities and their differences at $T = 298.15 \text{ K}$.

Compound	$C_{p,m}^\circ(\text{cr})$ Calc. $\text{J mol}^{-1} \text{ K}^{-1}$	$C_{p,m}^\circ(\text{cr})$ Exp. $\text{J mol}^{-1} \text{ K}^{-1}$	$-\Delta_{\text{cr}}^g C_{p,m}^\circ$ $\text{J mol}^{-1} \text{ K}^{-1}$
RDX	(259.2) ^a	248.9 [12]	38.1 ^c
TNX	214.8 ^b	n.a.	33.0 ^c

Values in parentheses were not used for calculation of molar heat capacity differences. n.a.: not available. ^a Derived from the molecular increments procedure described by Chickos *et al.* [15]. ^b Calculated according to the empirical increment approach by Hurst *et al.* [13]. ^c Calculated by $-\Delta_{\text{cr}}^g C_{p,m}^\circ = 0.75 + C_{p,m}^\circ(\text{cr}) \times 0.15$ [14].

3 Results and Discussion

3.1 RDX

The sublimation behavior of RDX was measured in the temperature range of 342.4 – 397.1 K. The absolute vapor pressures p_{sat} and thermodynamic properties of sublimation obtained by the transpiration method are compiled in Table 3. Several datasets of vapor pressures are available in the literature. A comparison of own data with literature experiments regarding the enthalpies of sublimation is compiled in Table 4. Figure 2 shows a *Clausius-Clapeyron* plot of the own and literature p - T data for the sublimation of RDX.

There have been several attempts to measure vapor pressures of RDX in the past. Some of the first reported experimental values were obtained by *Edwards* [16] by Knudsen effusion method and *Rosen and Dickinson* [17] by Langmuir effusion technique. In this work, the corresponding experimental p - T data from the works of *Edwards* [16] and *Rosen and Dickinson* [17] were used to derive enthalpies of sublimation at 298.15 K: $(114.8 \pm 5.4) \text{ kJ mol}^{-1}$ and $(131.8 \pm 3.5) \text{ kJ mol}^{-1}$, respectively.

In several studies, the vapor pressure of RDX was measured in order to prove validity of newly developed methods. The work by *John et al.* [18] applied isotopic dilution method. The fitting equation was obtained from vapor pressures at three temperatures and the resulting enthalpy of sublimation, 59.2 kJ mol^{-1} (derived in this work by equations 2 and 3) does not agree with any other reported literature data (see Table 4). Moreover, as mentioned in the report by *Östmark et al.* [2], the results in the provided graph do not match the reported fitting equation. *Hikal et al.* [19]

implemented an UV-absorbance technique on thin nano-films of common explosives (TNT and RDX). The measurements of RDX were conducted at two different wavelengths (209 and 243 nm) and they yielded different enthalpies of sublimation at 298.15 K. Furthermore, it is not clear which set of results was used to form the resulting fitting equation.

In 1978, *Cundall et al.* [23] reported a fitting equation for the vapor pressures of RDX in the temperature range from 343.4 to 447.4 K. Three years later a corrigendum was issued with corrected equation coefficients and the resulting enthalpy of sublimation is $137.8 \text{ kJ mol}^{-1}$. Another fitting equation of *R. Stimac* was reported as a personal communication in the study of *Eiceman et al.* [21]. The study reports that the experiment was conducted by adsorbing the vapors and analysing them by Ion Mobility Spectrometry (IMS). Unfortunately, no experimental temperature range is provided. The study of *Eiceman et al.* [21] calculated the values for three different temperatures and, in this work, we plot the corresponding fitting equation in this temperature range.

One of the most recent studies on the vapor pressures of the RDX is a study by *Felix-Rivera et al.* [20], conducted with isothermal thermogravimetric analysis (TGA). The work provides no experimental p - T data, solely a fitting equation of the relationship of mass loss vs. the temperature. The resulting enthalpy of sublimation, $101.9 \text{ kJ mol}^{-1}$, does not agree with the majority of the other literature values for reasons stated before [4a].

Deviations of experimental literature values from p - T equation derived from p - T data obtained in this work (Table 3) are illustrated in Figure 3.

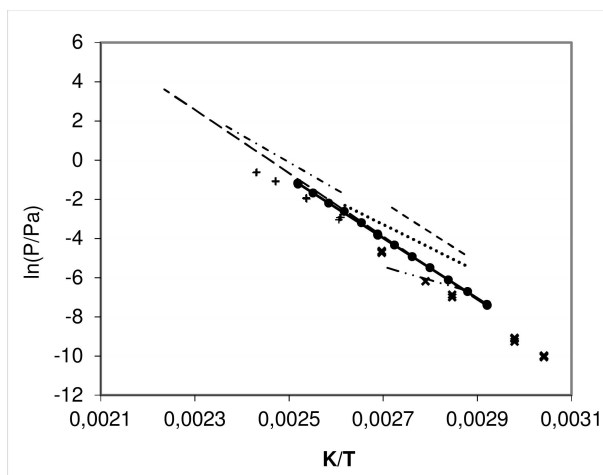


Figure 2. Experimental vapor pressure values of RDX in comparison with literature values. Here ● and solid line – from this work, --- line from *Felix-Rivera et al.* [20], - - - line from *Hikal et al.* [19], - · - · line from *R. Stimac* [21], — — line from *Cundall et al.* [22], - · · · line from *John et al.* [18], × from *Rosen and Dickinson* [17], + - from *Edwards* [16].

3.2 TNX

The sublimation behavior of TNX was measured in the temperature range of 312.6 – 357.1 K. The absolute vapor pressures p_{sat} and thermodynamic properties of sublimation obtained by the transpiration method are compiled in Table 3.

Only one experimental p - T dataset is available in the literature. A comparison of own data with the results of the work of *Pepekin et al.* [24] is presented in Table 5 and Figure 4. In the work of *Pepekin et al.* [24], vapor pressures were measured with the Knudsen effusion method in the temperature range from 325.2 to 360.2 K. No experimental p - T data was disclosed, solely a fitting equation without specifying the units of pressure and resulting calculated enthalpy of sublimation at average temperature was reported $(112.5 \pm 0.8 \text{ kJ mol}^{-1})$. In this work, we assume that the results were reported in Torr and Figure 4 depicts the differences between the vapor pressures measured in this work and the results from a fitting equation reported by *Pepekin et al.* [24].

Table 3. Absolute vapor pressures p_{sat} and thermodynamic properties of sublimation of RDX and TNX obtained by the transpiration method in this work.

RDX: $\Delta_{\text{cr}}^{\text{g}}H_m^{\circ}$ (298.15 K) = (130.9 ± 2.1) kJ mol ⁻¹								
$\ln \frac{p_{\text{sat}}}{p^{\circ}} = \frac{359.2}{R} - \frac{142206.8}{RT} - \frac{38.1}{R} \ln \frac{T}{298.15 \text{ K}}$								
$T_{\text{exp}}^{\text{a}}$	m^{b}	$V_{\text{N}_2}^{\text{c}}$	$T_{\text{amb}}^{\text{d}}$	Gasflow	$p_{\text{sat}}^{\text{e}}$	$u(p_{\text{sat}})^{\text{f}}$	$\Delta_{\text{cr}}^{\text{g}}H_m^{\circ}$	$\Delta_{\text{cr}}^{\text{g}}S_m^{\circ}$
[K]	[μg]	[dm ³]	[K]	[dm ³ h ⁻¹]	[mPa]	[mPa]	[kJ mol ⁻¹]	[J mol ⁻¹ K ⁻¹]
342.4	6.72	123	297.3	5.12	0.61	0.01	129.15	219.9
342.4	5.09	93.5	297.1	3.89	0.61	0.01	129.15	219.9
342.4	6.63	117	299.7	4.90	0.64	0.02	129.15	220.3
342.4	5.31	93.6	299.7	3.88	0.64	0.02	129.15	220.2
347.3	12.7	117	299.1	4.89	1.21	0.03	128.97	219.8
352.3	24.1	123	300.7	4.95	2.21	0.05	128.78	219.0
357.2	8.01	21.9	300.4	4.90	4.11	0.10	128.60	218.6
362.1	76.4	118	299.0	4.90	7.25	0.17	128.41	217.9
367.1	132	114	300.7	4.93	13.1	0.3	128.22	217.5
371.9	11.0	5.64	296.2	5.45	21.7	0.5	128.04	216.7
372.0	11.9	6.00	297.2	4.86	22.0	0.5	128.04	216.8
372.0	47.6	23.1	300.8	4.96	23.2	0.6	128.04	217.1
376.9	17.4	4.75	299.4	3.90	41.1	1.0	127.86	217.0
382.1	8.87	1.38	301.5	3.93	72.8	1.7	127.66	216.6
387.0	6.88	0.68	298.1	2.73	112	3	127.48	215.5
392.0	11.5	0.68	298.7	2.74	188	4	127.29	215.1
397.0	34.7	1.30	298.3	4.89	297	7	127.10	214.3
397.0	38.4	1.46	298.4	5.83	294	7	127.10	214.3
397.1	18.8	0.69	299.0	2.74	307	7	127.10	214.6
TNX: $\Delta_{\text{cr}}^{\text{g}}H_m^{\circ}$ (298.15 K) = (108.1 ± 1.6) kJ mol ⁻¹								
$\ln \frac{p_{\text{sat}}}{p^{\circ}} = \frac{336.5}{R} - \frac{117926.7}{RT} - \frac{33.0}{R} \ln \frac{T}{298.15 \text{ K}}$								
$T_{\text{exp}}^{\text{a}}$	m^{b}	$V_{\text{N}_2}^{\text{c}}$	$T_{\text{amb}}^{\text{d}}$	Gasflow	$p_{\text{sat}}^{\text{e}}$	$u(p_{\text{sat}})^{\text{f}}$	$\Delta_{\text{cr}}^{\text{g}}H_m^{\circ}$	$\Delta_{\text{cr}}^{\text{g}}S_m^{\circ}$
[K]	[mg]	[dm ³]	[K]	[dm ³ h ⁻¹]	[mPa]	[mPa]	[kJ mol ⁻¹]	[J mol ⁻¹ K ⁻¹]
312.6	0.04	82.8	296.1	3.50	6.13	0.13	107.62	206.2
312.6	0.03	78.7	296.4	4.85	6.14	0.13	107.62	206.2
317.7	0.07	80.5	296.3	4.81	11.9	0.2	107.45	205.6
322.6	0.03	19.0	296.4	4.84	21.9	0.5	107.29	205.1
327.6	0.22	75.1	296.3	4.84	40.6	0.8	107.13	204.7
332.5	0.05	9.35	296.4	4.84	72.7	1.5	106.97	204.2
337.4	0.04	4.75	296.4	4.83	130	3	106.80	203.9
337.4	0.05	5.40	296.2	4.83	128	3	106.80	203.7
337.4	0.04	4.76	296.4	4.84	129	3	106.80	203.8
342.3	0.05	3.40	297.4	4.86	217	4	106.64	203.1
347.2	0.05	2.01	297.6	4.83	376	8	106.48	202.8
352.1	0.05	1.21	296.3	4.84	637	13	106.32	202.5
357.0	0.09	1.21	296.3	4.84	1029	21	106.16	201.9
357.1	0.09	1.21	296.3	4.84	1045	22	106.15	201.9
357.1	0.09	1.21	296.4	4.85	1023	21	106.15	201.7
357.1	0.09	1.21	296.6	4.85	1009	21	106.15	201.6

^a Saturation temperature ($u(T) = 0.1 \text{ K}$). ^b Mass of transferred sample. ^c Volume of nitrogen ($u(V) = 0.005 \text{ dm}^3$) used to transfer m ($u(m) = 0.0001 \text{ g}$) of the sample. ^d T_{amb} is the temperature of the soap bubble meter used for measurement of the gas flow. ^e Vapor pressure at temperature T , calculated from the m and the residual vapor pressure at the condensation temperature calculated by an iteration procedure; $p^{\circ} = 1 \text{ Pa}$. ^f Expressed as standard uncertainties, more details are given in Supporting Information. Uncertainties of sublimation enthalpies are expressed as expanded uncertainties ($k = 2$) and they were derived according to the procedures reported in [11a,25].

Table 4. Compilation of data on enthalpies of sublimation $\Delta_{cr}^g H_m^\circ$ of RDX.

Experiment ^a	Method ^b	T-Range K	T_{avg} K	$\Delta_{cr}^g H_m^\circ(T_{avg})$ kJ mol ⁻¹	$\Delta_{cr}^g H_m^\circ(298.15\text{ K})^c$ kJ mol ⁻¹	p_{sat}^d μPa
Felix-Rivera <i>et al.</i> 2011 [20]	TGA, O	348.0–383.0	365.1	99.4	[101.9]	[13.67]
Hikal <i>et al.</i> 2011 [19]	UV, O	348.2–368.2	353.0	128.5	[130.8]	[4.42]
R. Stimac 1997 [21]	IMS, O	–	–	–	[118.8]	[5.36]
Cundall <i>et al.</i> 1981 [22] ^g	K, O	343.4–447.4	393.1	134.2	[137.8]	[0.45]
John <i>et al.</i> 1975 [18]	ID, O	347.2–369.2	357.6	56.9	[59.2]	[45.33]
Rosen <i>et al.</i> 1969 [17]	L	328.9–370.9	346.5	129.9	131.8 ± 3.5	0.31
Edwards 1953 [16]	K	383.2–411.7	398.7	111.1	114.8 ± 5.4	2.04
This Work	T	342.4–397.1	367.4	128.2	130.9 ± 2.1	0.71
					129.5 ± 1.7 ^e	1.02 ^f

Values in brackets were not used in further analysis. ^a First author and year of publication. ^b Methods: O: Equation only, T: Transpiration Method, TGA: Isothermal Thermogravimetric Method, K: Knudsen effusion, UV: UV-absorbance spectroscopy, IMS: Ion Mobility Spectroscopy, L: Langmuir Effusion, ID: Isotopic Dilution, IMS: Ion Mobility Spectrometry. ^c Enthalpies of sublimation were derived using the equation (3) and adjusted according to Chickos *et al.* [26]: $\Delta_{cr}^g C_{p,m}^\circ = 38.1\text{ J mol}^{-1}\text{ K}^{-1}$ from DCS measurement of $C_{p,m}^\circ(\text{cr}) = 248.9\text{ J mol}^{-1}\text{ K}^{-1}$ by Krien *et al.* [12]. Uncertainty for enthalpy of sublimation is expressed as expanded uncertainty with confidence level of 0.95 ($k=2$). ^d Vapor pressure at 298.15 K. ^e Weighted average value, calculated using uncertainty as the weighing factor. ^f Average value. ^g Corrigendum of work in 1978 [23].

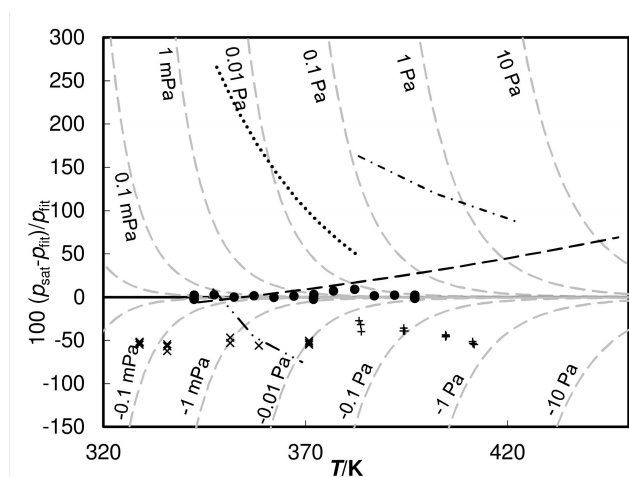


Figure 3. Experimental vapor pressure p_{sat} deviations from the derived fitting equation p_{fit} for RDX in Table 3. Here • and solid line – from this work, line from Felix-Rivera *et al.* [20], - - - line from R. Stimac [21], — — line from Cundall *et al.* [22], - · - · - line from John *et al.* [18], × – from Rosen and Dickinson [17], + – from Edwards [16]. Results from Hikal *et al.* [19] possess extremely big deviations from other literature results and, therefore, are not depicted in this graph.

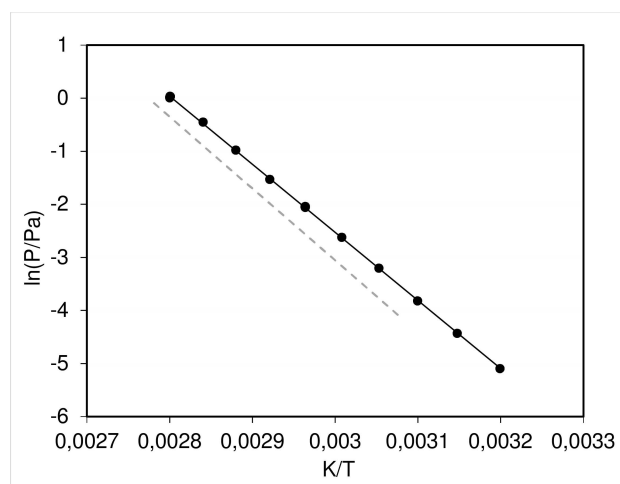


Figure 4. Experimental vapor pressure values of TNX in comparison with literature values. Here • and solid line – from this work, dashed grey line – from Pepekin *et al.* [24].

Table 5. Compilation of data on enthalpies of sublimation $\Delta_{cr}^g H_m^\circ$ of TNX.

Experiment ^a	Method ^b	T-Range K	T_{avg} K	$\Delta_{cr}^g H_m^\circ(T_{avg})$ kJ mol ⁻¹	$\Delta_{cr}^g H_m^\circ(298.15\text{ K})^c$ kJ mol ⁻¹	p_{sat}^d μPa
Pepekin <i>et al.</i> 1974 [24]	K, O	325.2–360.2	342.3	112.6	114.0	376
This Work	T	312.6–357.1	337.3	106.9	108.1 ± 1.6	823

^a First author and year of publication. ^b Methods: T: Transpiration, K: Knudsen effusion, O: Equation only. ^c Enthalpies of sublimation were derived using the equation (3) and adjusted according to Chickos *et al.* [14] with values of $\Delta_{cr}^g C_{p,m}^\circ$ and $C_{p,m}^\circ(\text{cr})$, stated in Table 2. Uncertainty for enthalpy of sublimation is expressed as expanded uncertainty with confidence level of 0.95 ($k=2$). ^d Vapor pressure at 298.15 K.

4 Conclusion

In this study, new experimental vapor pressures for one of the most commonly used explosive RDX and its environmental decomposition product TNX, which is also known as common homemade explosive, were measured using the transpiration method. p - T fitting equations for RDX in the temperature range from 342.4 to 397.1 K and TNX in the temperature range from 312.6 to 357.0 K are also reported. These equations were extrapolated to yield vapor pressures and enthalpies of sublimation at ambient conditions ($0.71 \mu\text{Pa}$, $(130.9 \pm 2.1) \text{ kJ mol}^{-1}$ for RDX; $823 \mu\text{Pa}$, $(108.1 \pm 1.6) \text{ kJ mol}^{-1}$ for TNX). Results were compared with existing p - T data in the literature. In case of RDX, several data sets are available, however, most of the vapor pressure data is inconsistent. This could be associated with the fact that RDX is extremely low-volatile. New reported experimental vapor pressures should introduce more certainty in the thermodynamic description of this important compound. As for TNX, only one set of experimental vapor pressures has been recorded in the past and the results considerably differ. Since the vapor pressures of TNX are significantly higher than of its mother compound, it could allow more efficient detection of the past or current presence of explosive RDX in environmental conditions.

Acknowledgements

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