

# Gas-phase Concentration of Triacetone Triperoxide (TATP) and Diacetone Diperoxide (DADP)

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**Abstract:** The present investigation is about the determination of the gas phase concentration parameters of the notorious explosives triacetone triperoxide (TATP, **1**) and diacetone diperoxide (DADP, **2**), which have been frequently used in improvised explosive devices. According to calculations with EXPLO5 the energetic performance of both explosives is similar. The enthalpy of sublimation  $\Delta_{cr}^{\circ}H_m^{\circ}$  (298.15 K) (**1**:  $76.7 \pm 0.7$  kJ mol<sup>-1</sup>; **2**:  $75.0 \pm 0.5$  kJ mol<sup>-1</sup>) and vapor pressures  $p_{sat}$ (298.15 K) (**1**: 6.7 Pa, **2**: 26.6 Pa) of both compounds have been studied using the transpiration method in the ambient temperature range of 274–314 K. The results obtained in this work were compared critically

with the existing literature values. Data for DADP (**2**) mostly shows agreement with literature ones. However data of TATP (**1**) obtained in this work revealed insufficient agreement of all sets of data available in literature, which might be explained by the rich polymorphism of TATP **1**. The saturation and diffusion equilibrium concentration of both analytes was calculated at 298.15 K. In comparison to the saturation equilibrium concentration measured in this work (**1**: 600 µg L<sup>-1</sup>, **2**: 1589 µg L<sup>-1</sup>) the corresponding estimated diffusion condition air concentrations (**1**: 3.1 ng L<sup>-1</sup>, **2**: 10 ng L<sup>-1</sup>, for a surface of 200 cm<sup>2</sup>) are lower by five orders of magnitude.

**Keywords:** Peroxides • Vapor Pressure • Energetic Materials • Air Concentration • Explosive Detection

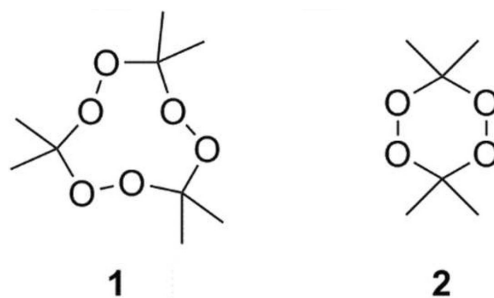
## 1 Introduction

Triacetone triperoxide (**1**), also known as TATP, is the condensation product of hydrogen peroxide with acetone and was discovered accidentally by *Wolffenstein* [1] in 1895.

Due to its high volatility and sensitivity toward external stimuli the medium performance explosive is not applied in neither the civil nor the military sector.

With respect to the free availability of its precursors and its readiness for detonation initiation the compound is popular in the amateur chemist and terrorist scene. Unfortunately this was demonstrated by the recent TATP related incident in Oberursel (Germany, 2015, [2]) and the ISIS terror attack in Paris (France, 2015, [3]). A 17 year old teenager (Germany, 2006, [4]) was arrested for hoarding 2 kg of TATP **1**, which underlines the ease of TATP **1** synthesis. *Oxley et al.* investigated the factors influencing the formation of TATP **1** and its side product diacetone diperoxide (DADP, **2**) [5] as well as the destruction of TATP [6]. *Lubczyk et al.* [7] recently published a method for desensitizing TATP for training and testing purposes in an ionic liquid matrix and pointed out that resublimed TATP **1** shows a higher impact (0.1 J) and friction sensitivity of (0.05 N) than the crude product from the aqueous synthesis (0.5 J, 0.2 N) that is stabilized by trace amounts of water. The resublimation of TATP during storage enhances the risk of unintended detonation. With respect to this and the challenging gas phase detection of explosives [8] one of the most interesting parameters of TATP and DADP is their vapor pressure. The sublimation behavior of both peroxides **1** and **2** was meas-

ured in this work with the transpiration method and compared critically with the existing literature data. Recommendations for the ambient condition (298.15 K) vapor pressure, saturation and diffusion equilibrium air concentration and enthalpy of sublimation are given (Figure 1).



**Figure 1.** Chemical structures of TATP **1** and DADP **2**.

## 2 Experimental

All reagents and solvents were used as received (Sigma-Aldrich, Fluka, Acros Organics, ACBR). NMR spectra were

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measured with a JEOL ECX-400 and a Bruker AVANCE 400 MHz NMR instrument. The chemical shift of the solvent peaks were adjusted according to literature values [38]. Infrared spectra were measured with a Perkin-Elmer FT-IR Spektrum BXII instrument equipped with a Smith Dura SamplIR II ATR unit. Transmittance values are described as "strong" (s), "medium" (m), and "weak" (w). Raman spectra were recorded on a Bruker RAM II device (1064 nm, 300 mW). Relative peak intensities are given in brackets. Elemental analyses (EA) were performed with a Netzsch STA 429 simultaneous thermal analyzer. Sensitivity data were determined using a BAM drophammer and a BAM friction tester. The electrostatic sensitivity tests were carried out using an Electric Spark Tester ESD 2010 EN (OZM Research). The particle sizes stated are valid for all sensitivity measurements. Melting points were measured with a Buechi B-540 melting point apparatus using a heating rate of  $5^{\circ}\text{C min}^{-1}$ . For the powder diffraction experiment on TATP the analytes were filled into a 0.5 mm Lindemann capillary. The material was then investigated on a Huber G644 Guinier diffractometer with the angle calibrated using electronic grade germanium ( $a=5.6575\text{ \AA}$ ). Measurements with  $\text{MoK}_{\alpha 1}$  radiation were made over the  $2\theta$  range  $2\text{--}12^{\circ}$  with an increment of  $0.02^{\circ}$  and a counting time of 20 seconds per increment at  $25^{\circ}\text{C}$ .

**CAUTION! TATP 1 and DADP 2 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 earthed equipment) should be used during the handling of both compounds at all times including vapor pressure measurements.**

**TATP 1:** 3.14 mL 50% aqueous  $\text{H}_2\text{O}_2$  solution (3.76 g, 0.11 mol) and 0.86 mL conc.  $\text{H}_2\text{SO}_4$  (1.58 g, 0.016 mol) are mixed and cooled to  $0^{\circ}\text{C}$ . 4.90 mL acetone (3.87 g, 0.07 mol) are added dropwise. After stirring the mixture at  $0^{\circ}\text{C}$  for 3 h, it is extracted with 70 mL pentane. The pentane mixture is washed two times with 20 mL saturated ammonium sulfate solution and afterwards three times with 20 mL of water. The organic phase is dried over magnesium sulfate. After evaporation of the solvent a colorless solid is isolated. (2.07 g, 40%) [9]

**$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 400 MHz, 300 K):  $\delta=1.45$  (18 H).  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 100 MHz, 300 K):  $\delta=21.5$  ( $\text{CH}_3$ ), 107.7 (C). **IR** (ATR):  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 3005 (w), 2945 (w), 1600 (w), 1461 (w), 1376 (m), 1361 (m), 1274 (w), 1232 (m), 1200 (m), 1178 (s), 997 (w), 945 (m), 937 (m), 884 (s), 842 (m), 784 (m), 615 (m). **Raman** (1064 nm)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 3012 (55), 3001 (54), 2948 (100), 10450 (30), 1372 (5), 1338 (6), 962 (48), 913 (50), 864 (60), 856 (48), 653 (7), 555 (61), 452 (28), 434 (30), 412 (28), 380 (8). **EA** found (calcd.): C 48.73 (48.63), H: 8.26 (8.18). **IS:** 1.5 J, **FS:** < 5 N, **ESD:** 0.2 J (< 100  $\mu\text{m}$ ),  **$T_{\text{melt}}$ :** 97–98  $^{\circ}\text{C}$ .

**DADP 2:** 10 mL dichloromethane are cooled in an ice bath. 2.00 mL acetone (1.58 g, 0.03 mol) and 4.00 mL 30% aqueous  $\text{H}_2\text{O}_2$  solution (4.44 g, 0.04 mol) are added. 4.00 mL concentrated perchloric acid (7.08 g, 0.07 mol) are added

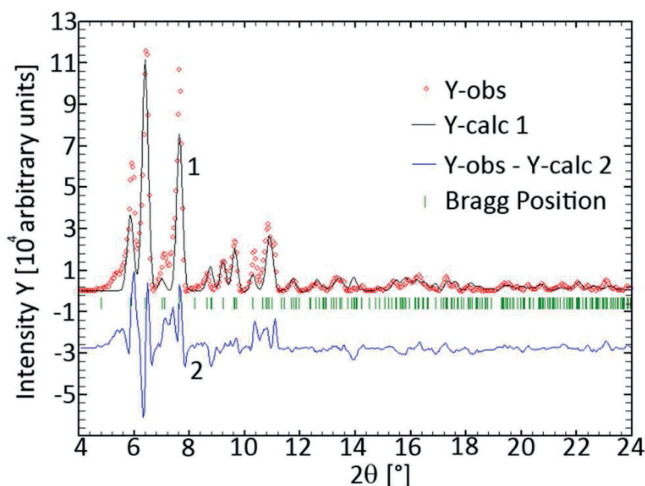
drop wisely and the mixture was stirred at  $0^{\circ}\text{C}$  for 1 h. Afterwards the mixture is stored for three days at room temperature to allow complete conversion of TATP to DADP. The formed colorless precipitate is filtered off, washed with water and recrystallized from methanol. (0.23 g, 10%) [10].

**$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 400 MHz, 300 K):  $\delta=1.35$  (s, 6H), 1.79 (s, 6H).  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 100 MHz, 300 K):  $\delta=20.7$  ( $\text{CH}_3$ ), 22.5 ( $\text{CH}_3$ ), 107.7 (C). **IR** (ATR):  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 3031 (w), 3000 (w), 2955 (w), 1603 (w), 1452 (w), 1374 (m), 1367 (m), 1284 (w), 1268 (m), 1198 (s), 1006 (w), 943 (m), 930 (m), 858 (m), 839 (w), 814 (m), 686 (m). **Raman** (1064 nm)  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 3053 (25), 3004 (100), 2980 (62), 1450 (18), 1417 (21), 1260 (17), 940 (23), 917 (19), 863 (64), 720 (65), 512 (8), 501 (58), 491 (22), 452 (10), 447 (9), 428 (17), 382 (53). **EA** found (calcd.): C 48.24 (48.63), H: 8.13 (8.18), **IS:** 5 J, **FS:** 5 N, **ESD:** 0.2 J (< 100  $\mu\text{m}$ ),  **$T_{\text{melt}}$ :** 132–133  $^{\circ}\text{C}$ .

### 3 Results and Discussion

#### 3.1 Polymorphism of TATP

TATP was synthesized according to Milas *et al.* [9]. DADP was synthesized according to Landenberger *et al.* [10]. The complete chemical characterization of both compounds can be found in the experimental section. With respect to the six possible solid state polymorphs of TATP reported with crystal structures by Reany *et al.* [11] the TATP synthesized in this work was analyzed with powder X-Ray diffraction to determine its polymorphic composition (see Figure 2). It could be found that the investigated TATP consisted mainly of the main polymorph reported for TATP crude products



**Figure 2.** Powder diffractogram of the TATP synthesized in this work after Rietveld Refinement in comparison with the calculated diffractogram of the major polymorph (Cif-File #241973, [11–12]) found in TATP crude products. Y-obs: observed reflexes, Y-calc: calculated reflexes, Y-obs – Y-calc: difference of observed and calculated reflexes.

**Table 1.** Selected energetic parameters and relevant properties of crystalline TATP and DADP synthesized in this work in comparison with crystalline TNT.

	TATP 1	DADP 2	TNT
Formula	$C_9H_{18}O_6$	$C_6H_{12}O_4$	$C_7H_5N_3O_6$
MW/g mol <sup>-1</sup>	222.24	148.16	227.13
$IS^{[a]}/J$	1.5	5	15
$FS^{[b]}/N$	< 5	5	> 360
$ESD^{[c]}/mJ$	0.2	0.2	0.7
Grain Size/ $\mu m$	< 100	< 100	100-500
$\Omega_{CO}; \Omega_{CO_2}/\%$ <sup>[d]</sup>	-86.4; -151.2	-86.4; -151.2	-24.7; -74.0
$T_m^{[e]}/^{\circ}C$	97-98	132-133	80-81
$\rho^{[f]}/g\ cm^{-3}$	1.27 [180 K] [15]	1.33 [208 K] [16]	1.71 [100 K]
$\rho_{298K}^{[g]}/g\ cm^{-3}$	1.25 [298 K]*	1.31 [298 K]*	1.66 [298 K]*
$\Delta_f H^{[h]}/kJ\ mol^{-1}$	-640	-435	-54
$\Delta_f U^{[i]}/kJ\ kg^{-1}$	-2744	-2802	-163
EXPLO5 v6.03 values (calculated for $\rho_{298K}^{[g]}$ of crystalline material)			
$-\Delta_{ex} U^{[k]}/kJ\ kg^{-1}$	3420	73194	4425
$p_{CJ}^{[j]}/[10^8\ Pa]$	114	131	191
$V_{det}^{[m]}/m\ s^{-1}$	6322	6246	6906
$V_0^{[n]}/L\ kg^{-1}$	821	815	642

[a] impact sensitivity, BAM drophammer (method 1 of 6); [b] friction sensitivity, BAM friction tester (method 1 of 6); [c] sensitivity toward electrostatic discharge; [d] oxygen balance; [e] melting point range ( $5^{\circ}C\ min^{-1}$ , glass capillary); [f] density from X-Ray diffraction; [g] density at 298 K (calculated using the equation ( $\rho_{298K} = \rho_T / (1 + \alpha_V(298 - T_0))$ ;  $\alpha_V = 1.5 \cdot 10^{-4}\ K^{-1}$ ); [h] calculated heat of formation (CBS-4M); [i] calculated energy of formation (CBS-4M); [j] heat of detonation; [k] detonation pressure; [l] detonation velocity; [m] volume of gases after detonation.

(Cif-File #241973, [11–12]). The discrepancies between the observed and calculated diffractograms can be explained by the presence of further unknown polymorphs.

### 3.2 Sensitivities and Energetic Properties

Table 1 gives an overview about the energetic properties and other selected parameters of TATP and DADP synthesized in this work and the melt-cast explosive 2,4,6-trinitrotoluene (TNT) for comparison. TATP is very sensitive, while DADP is less sensitive toward impact. Both peroxides are extremely sensitive toward friction. [13] The sensitivity values for TATP are slightly higher than the values stated by Lubczyk *et al.* [7], yet the friction sensitivity measured in this work is at the lower limit of the measurement range of the testing device used (5 N). Both compounds have 200 mJ sensitivity toward electrostatic discharge. With a room temperature density of  $1.25\ g\ cm^{-3}$  (see Table 1) the nine-membered ring system TATP is less dense than the six-membered DADP ( $1.31\ g\ cm^{-3}$ ). The denser crystal packing in DADP results in the higher melting point range (heating rate  $5^{\circ}C\ min^{-1}$ ) of  $132\text{--}133^{\circ}C$  in comparison to  $97\text{--}98^{\circ}C$  for TATP. The exothermic enthalpies of formation of both compounds (**1**:  $-640\ kJ\ mol^{-1}$ ; **2**:  $-435\ kJ\ mol^{-1}$ ) were calculated on a CBS-4 M level using the *Gaussian 09* [14] software. Based on these values and the theoretical maximum density at 298 K the energetic characteristics were calculated using EXPLO5 v6.03 (BKW EOS, BKWN constants, initial temperature 3600 K). Both peroxides have a similar theoretical detonation pressure  $p_{CJ}$  (**1**:  $114 \times 10^8\ Pa$ , **2**:  $131 \times 10^8\ Pa$ ) and

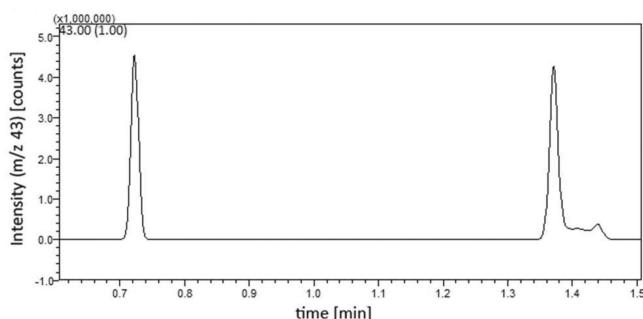
detonation velocity  $V_{det}$  (**1**:  $6322\ m\ s^{-1}$ , **2**:  $6246\ m\ s^{-1}$ ). When compared to crystalline TNT ( $p_{CJ}$ :  $191 \times 10^8\ Pa$ ,  $V_{det}$ :  $6906\ m\ s^{-1}$ ), the energetic performance of both peroxides is lower.

### 3.3 VO-GC/MS of TATP and DADP

TATP and DADP were analyzed using vacuum outlet gas chromatography as established by de Zeeuw *et al.* [17] using a Shimadzu GC/MS QP2010 SE device equipped with an Atas Optic 4 injector and a Shimadzu AOC-20i autosampler. The necessary restriction (10.1 mm length, 0.05 mm inner diameter, Restek® cat. #10098) was connected to a Restek® RTX TNT 1 column (cat. #12998) with a SGE Siltite®  $\mu$ -Union (cat. #073562) inside the injector. Due to the incompatibility of the inner diameter of the commercially available Atas liners a custom V2A stainless steel liner (10 mm length, 5 mm outer diameter, 0.5 mm wall thickness, split notches at bottom end) was used. Both the liner and the  $\mu$ -union were inertized with a Silconert® 2000 coating. The injector was operated at  $175^{\circ}C$  in the constant pressure mode with a head pressure of 90 kPa Helium 5.0 carrier gas and a split ratio of 150 in combination with a virtual column (100 m length, 0.25  $\mu m$  film thickness, 0.20 mm diameter) for the LabSolutions GCMS Solution Software. The injection volume was 1  $\mu L$ . The GC oven program start temperature was  $30^{\circ}C$  with a hold time of 6 seconds followed by a temperature ramp to  $204^{\circ}C$  with  $60^{\circ}C\ min^{-1}$ . The temperature of the MS-Interface and the ion source was  $200^{\circ}C$ . The mass spectrometer was operated in the single ion monitoring mode

with an event time of 0.10 s and a micro scan width of 0.1 amu. From 0.50 to 2.00 min the mass channels 43, 59, 58 and 75 were monitored for the detection of the peroxides **1** and **2**. From 2.00 to 3.00 min the mass channels 57, 43, 71 and 85 were monitored for the detection of *n*-dodecane C-12 as analytical standard in quantification applications.

Figure 3 shows a chromatogram of TATP and DADP in *tert*-butyl methyl ether using the method stated before. DADP elutes after 0.72 min at 67 °C as a single peak whilst one TATP conformer A elutes after 1.37 min at 106 °C and a second TATP conformer B elutes after 1.44 min at 110 °C. The augmented baseline between both conformers indicates the conversion of conformer A to the more stable conformer B during the GC/MS analysis. The solid state polymorphism of TATP has been reported before [11] and two isomers of TATP have been separated by LC-NMR [18]. The activation barrier of an exothermic TATP polymorph interconversion has been calculated to be 110 kJ mol<sup>-1</sup> [19]. With respect to this the GC/MS behavior of TATP observed in this work can be justified. Both TATP ( $R^2=0.99995$ ) and DADP ( $R^2=0.9998$ ) could be excellently quantified in concentrations of 20 to 60 µg/mL with an internal standard (C-12) method using the GC/MS configuration detailed above.



**Figure 3.** SIM mode (m/z 43) GC/MS chromatogram of TATP (right) and DADP (left).

### 3.4 Vapor Pressure Measurement

Since the vapor pressure of a compound is the key parameter for its gas phase detectability the vapor pressure of TATP and DADP was measured in this work using the transpiration method. The transpiration method setup adapted in this work has been established by Verevkin *et al.* [20]. For the experiments in this work nitrogen (99.999% purity) was used as carrier gas. The flow-rate ranging from 1–3 L h<sup>-1</sup> was adjusted and kept constant using a mass flow controller (Natec Sensors MC-100 CCM). The gas flow is conducted through the saturator, which is a glass vessel surrounding a U-shaped tube (8 mm inner diameter, 50 cm length) and containing a thermofluid, which is pumped through the saturator vessel with a circulation thermostat

(Huber Ministat 230 with external class A PT-100 temperature sensor inside the saturator vessel). The peroxide (0.8 g) is coated on glass beads (1 mm diameter, 40 g) and filled into the saturator tube. For the coating of the glass beads with the sensitive peroxide explosives they were dispersed in a minimum amount of *n*-pentane and the resulting slurry filled into the saturator tube followed by removal of the *n*-pentane by application of the carrier gas stream at room temperature. After leaving the saturator and reaching the saturation equilibrium with the analyte the carrier gas stream is conducted through a condenser tube, which is positioned in a dewar vessel containing *iso*-propanol that is cooled to –30 °C by an immersion cooler (Huber TC45E). The exact carrier gas flow-rate is measured with a soap film flow meter (Hewlett Packard No.: 0101–0113) and the ambient temperature is recorded for the volume measurement (Greisinger GFTB 200) for each datapoint. The time frame from insertion of the condenser tube into the saturator to its removal was measured for the calculation of the total volume of carrier gas. After its removal from the saturator the condenser tube was closed at both ends and *tert*-butyl methyl ether solvent was filled into it containing a known amount of *n*-dodecane as internal standard for the subsequent GC/MS quantification. With the temperature of the saturator  $T_{exp}$ , the mass of the analyte trapped in the condenser tube  $m_a$ , the ambient temperature  $T_{amb}$  and the volume of carrier gas measured at ambient conditions  $V_{amb}$  the vapor pressure  $p_{sat}$  of the analyte can be calculated. The calculation of the vapor pressure relies on the Ideal Gas Law, the Dalton's Law of partial pressures and the assumption that the volume of the gaseous analyte is negligibly small in comparison to that of the carrier gas:

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

$p_{sat}$ : 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<sup>3</sup>],  $M$ : molecular weight of the analyte [kg mol<sup>-1</sup>],  $R$ : universal gas constant: 8.3145 J mol<sup>-1</sup> K<sup>-1</sup>

The obtained values of the experimental vapor pressure  $p_{sat}$  at the saturator temperature  $T_{exp}$  are processed mathematically with a fitting function that is based on the *Clarke-Glew* equation [21]:

$$\ln p_{sat}/p^0 - \frac{\Delta_{cr}^g C_{p,m}^0}{R} \ln \frac{T}{T_0} = A - \frac{B}{T} \quad (2)$$

$p^0$ : reference pressure (1 Pa),  $\Delta_{cr}^g C_{p,m}^0$ : heat capacity difference from crystalline to gaseous state [J mol<sup>-1</sup> K<sup>-1</sup>],  $T$ : temperature [K],  $T_0$ : reference temperature [K], A/B: fitting coefficients (A: [ ], B: [K]).

The enthalpy of sublimation at the temperature  $T$  is calculated by:

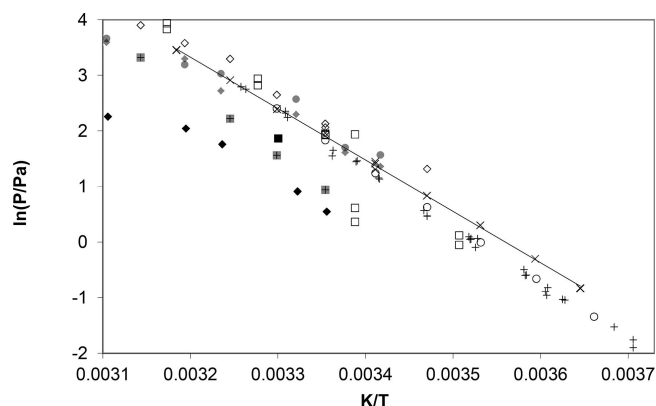
$$\Delta_{cr}^g H_m^o(T) = RB + \Delta_{cr}^g C_{p,m}^o T \quad (3)$$

$\Delta_{cr}^g H_m^o(T)$ : molar enthalpy of sublimation at temperature  $T$  [ $\text{J mol}^{-1}$ ]

The experimental heat capacities  $C_{p,m}^o$  (cf. Table 5) of both peroxides at room temperature were reported by Pilar *et al.* [22] and are in good agreement with the values calculated by the empiric elemental composition approached by Hurst *et al.* [23] ( $C_{p,m}^o$  (cr, 298.15 (calculated/experimental) [ $\text{J mol}^{-1} \text{K}^{-1}$ ], 1: 314.6/271.8, 2: 209.7/223.4). In this work the experimental values were used and the corresponding heat capacity differences  $\Delta_{cr}^g C_{p,m}^o$  calculated according to Chickos *et al.* [24]. The method for the calculation of the sublimation enthalpy and its uncertainty is described elsewhere [20b]. The available literature vapor pressure data for TATP and DADP was also collected. In some works the sublimation enthalpy was not derived from the vapor pressures or it was carried out in a different manner. In this work the literature vapor pressures were treated with equations (2) and (3) and the corresponding uncertainties were estimated according to [20b]. The obtained enthalpies of sublimation and vapor pressures at 298.15 K are compiled in comparison with our results in Table 4.

For TATP a value for  $\Delta_{cr}^g H_m^o(298.15 \text{ K})$  of  $76.7 \pm 0.7 \text{ kJ mol}^{-1}$  and a vapor pressure  $p_{sat}(298.15 \text{ K})$  of 6.7 Pa and for DADP a value for  $\Delta_{cr}^g H_m^o(298.15 \text{ K})$  of  $75.0 \pm 0.5 \text{ kJ mol}^{-1}$  and a vapor pressure  $p_{sat}(298.15 \text{ K})$  of 26.6 Pa was derived from the data obtained with the transpiration method in this work. (cf. Table 2)

The sublimation behavior of TATP was studied in this work in the temperature range from 274.3–314.1 K. The absolute vapor pressures  $p_{sat}$  and thermodynamic properties of sublimation obtained by the transpiration method in this work for TATP are compiled in Table 2. A comparison our of own data with literature experiments regarding the enthalpies of sublimation is compiled in Table 4, Figure 4



**Figure 4.** Experimental vapor pressure of TATP in comparison with literature values.  $\times$  this work, grey circle [25] (HCl), grey diamond [25] ( $\text{H}_2\text{SO}_4$ ), black diamond [27], black square [34], + [30], black triangle [28], white diamond [26a], white circle [32], grey + [29], white square [26b]. Linear regression line for this work.

shows a Clausius-Clapeyron plot of the own and literature p-T data for the sublimation of TATP. Available p-T literature data for comparison are four headspace gas chromatography measurements by Mbah *et al.* [25] and Oxley *et al.* [26], three thermogravimetric measurements by Mbah *et al.* [27], Oxley *et al.* [28] and Rivera *et al.* [29], one static method measurement by Egorshv *et al.* [30], a Knudsen-effusion measurement by Damour *et al.* [31] and a Quantum Cascade Laser Photoacoustic Spectroscopy measurement by Dunayevskiy *et al.* [32]. The thermogravimetric analysis (TGA) measurements may result in correct enthalpies of sublimation, yet they need to be calibrated with a reference material for the derivation of correct pressure values from the data measured. It has not been proven that this reference material calibration is suitable for a precise measurement of absolute vapor pressures. Therefore TGA measurements will be disregarded in the discussion of absolute vapor pressures. The data published by Dunayevskiy *et al.* [32] have been scaled to a measurement by Oxley *et al.* [26b]. Dunayevskiy *et al.* [32] published solely a p-T-equation of their data combined with that of Oxley *et al.* [26b] and no discrete pressure analog-temperature values which would allow fitting to other sets of data. Additionally it was mentioned by Damour *et al.* [31] that the dataset provided by Dunayevskiy *et al.* [32] seems to be systematically erroneous in the low temperature regime and needs to be cut. Therefore the data published by Dunayevskiy *et al.* [32] is excluded from the calculation of average values. Mbah *et al.* [25] measured TATP crude products that were synthesized under acid catalysis with hydrochloric and sulfuric acid. The crude product synthesized with sulfuric acid contained a large fraction of DADP impurity and therefore its measurement is disregarded in the calculation of average values and the discussion of measurement results.

Regarding the enthalpies of sublimation  $\Delta_{cr}^g H_m^o$  that were adjusted to 298.15 K (cf. Table 4) it becomes obvious that the values spread from  $68.0 \pm 6.3 \text{ kJ mol}^{-1}$  derived from the data reported by Mbah *et al.* [27] to  $103.8 \pm 6.4 \text{ kJ mol}^{-1}$  derived from the data reported by Oxley *et al.* [26b]. The scattering of the measurement values may be explained by the polymorphism of TATP reported by Reany *et al.* [11]. It was demonstrated that crude products of TATP contain one major and two minor mass fraction polymorphs of TATP and three additional polymorphs can be synthesized by recrystallization in organic solvents (hexane, tetrachloromethane, ethanol). Four of these polymorphs were analyzed by differential scanning calorimetry with reported sublimation enthalpies ranging from  $14.6 \text{ kJ mol}^{-1}$  at  $93.6^\circ \text{C}$  onset temperature to  $77.2 \text{ kJ mol}^{-1}$  at  $91.6^\circ \text{C}$  onset temperature. A sublimation enthalpy of  $14.6 \text{ kJ mol}^{-1}$  is not in accordance with the values measured by other methods for the TATP molecule (cf. Table 4). Despite that it cannot be neglected that polymorphism influences the sublimation behavior of TATP. It cannot be excluded that all measurements discussed in this work were measurements of polymorph mixtures or different pure polymorphs of 1. The relevant in-



**Table 2.** TATP: absolute vapor pressures  $p_{\text{sat}}$  and thermodynamic properties of sublimation obtained by the transpiration method in this workTATP:  $\Delta_{\text{cr}}^{\text{g}} H_m^{\circ}$  (298.15 K) =  $76.7 \pm 0.7 \text{ kJ mol}^{-1}$ 

$$\ln p_{\text{sat}}^{\text{a}}/p^{\circ} = \frac{314.7}{R} - \frac{89091.1}{RT} + \frac{41.5}{R} \ln \frac{T}{298.15 \text{ K}}$$

$T_{\text{exp}}^{\text{a}}$ [K]	$m_a^{\text{b}}$ [mg]	$V_{\text{N}_2}^{\text{c}}$ [dm <sup>3</sup> ]	$T_{\text{amb}}^{\text{d}}$ [K]	Gasflow [dm <sup>3</sup> h <sup>-1</sup> ]	$p_{\text{sat}}^{\text{e}}$ [Pa]	$u(p_{\text{sat}})^{\text{f}}$ [Pa]	$\Delta_{\text{cr}}^{\text{g}} H_m^{\circ}$ [kJ mol <sup>-1</sup> ]	$\Delta_{\text{cr}}^{\text{g}} S_m^{\circ}$ [J mol <sup>-1</sup> K <sup>-1</sup> ]
274.3	0.11	2.80	296.6	2.58	0.43	0.02	77.71	180.6
274.4	0.09	2.43	296.5	1.62	0.44	0.02	77.71	180.6
278.3	0.11	1.65	296.5	1.62	0.74	0.02	77.54	180.4
283.2	0.11	0.926	296.4	2.14	1.4	0.0	77.34	179.9
288.2	0.24	1.16	296.9	2.17	2.3	0.1	77.13	178.9
293.2	0.23	0.610	296.5	2.15	4.2	0.1	76.92	178.7
293.2	0.23	0.611	297.1	2.16	4.1	0.1	76.92	178.4
298.2	0.57	0.898	297.0	2.15	7.1	0.2	76.72	177.9
293.2	0.20	0.613	296.5	2.16	3.7	0.1	76.92	177.5
303.1	0.53	0.538	296.8	2.15	10.9	0.3	76.51	176.5
308.1	1.25	0.751	296.3	2.15	18.4	0.5	76.30	176.1
314.1	1.55	0.540	296.7	2.16	31.8	0.8	76.06	175.2
314.1	1.54	0.538	296.3	2.15	31.7	0.8	76.06	175.2
314.1	1.53	0.539	296.7	2.16	31.5	0.8	76.06	175.1

DADP:  $\Delta_{\text{cr}}^{\text{g}} H_m^{\circ}$  (298.15 K) =  $75.0 \pm 0.5 \text{ kJ mol}^{-1}$ 

$$\ln p_{\text{sat}}^{\text{a}}/p^{\circ} = \frac{313.2}{R} - \frac{85244.0}{RT} + \frac{34.3}{R} \ln \frac{T}{298.15 \text{ K}}$$

$T_{\text{exp}}^{\text{a}}$ [K]	$m_a^{\text{b}}$ [mg]	$V_{\text{N}_2}^{\text{c}}$ [dm <sup>3</sup> ]	$T_{\text{amb}}^{\text{d}}$ [K]	Gasflow [dm <sup>3</sup> h <sup>-1</sup> ]	$p_{\text{sat}}^{\text{e}}$ [Pa]	$u(p_{\text{sat}})^{\text{f}}$ [Pa]	$\Delta_{\text{cr}}^{\text{g}} H_m^{\circ}$ [kJ mol <sup>-1</sup> ]	$\Delta_{\text{cr}}^{\text{g}} S_m^{\circ}$ [J mol <sup>-1</sup> K <sup>-1</sup> ]
274.7	0.16	1.38	296.6	2.02	1.98	0.05	75.82	186.0
274.7	0.15	1.27	296.6	1.52	1.95	0.05	75.82	185.8
278.5	0.16	0.862	296.6	1.52	3.13	0.08	75.69	185.6
288.3	0.38	0.635	296.4	2.01	9.95	0.27	75.36	184.8
283.4	0.34	1.07	296.5	2.01	5.36	0.16	75.52	184.8
293.3	0.74	0.740	296.8	2.02	16.6	0.44	75.18	184.0
293.3	0.72	0.740	296.3	2.02	16.3	0.43	75.19	183.9
293.3	0.69	0.741	296.6	2.02	15.6	0.42	75.19	183.5
298.2	1.33	0.805	296.9	2.01	27.6	0.71	75.02	183.4
293.3	0.68	0.739	297.1	2.02	15.4	0.41	75.19	183.4
303.2	1.29	0.501	297.2	2.00	43.0	1.10	74.85	182.4
308.1	3.78	0.871	297.5	2.01	72.4	1.84	74.68	182.2
314.1	3.70	0.499	296.5	1.99	123	3.11	74.47	181.4
314.1	3.45	0.467	297.0	2.00	123	3.11	74.47	181.4
314.1	3.59	0.500	296.7	2.00	120	3.02	74.47	181.2

<sup>a</sup> Saturation temperature ( $u(T) = 0.1 \text{ K}$ ). <sup>b</sup> Mass of transferred sample condensed at  $T = 243 \text{ K}$ . <sup>c</sup> Volume of nitrogen ( $u(V) = 0.005 \text{ dm}^3$ ) used to transfer  $m$  ( $u(m) = 0.0001 \text{ g}$ ) of the sample. <sup>d</sup>  $T_a$  is the temperature of the soap bubble meter used for measurement of the gas flow. <sup>e</sup> Vapor pressure at temperature  $T$ , calculated from the  $m$  and the residual vapor pressure at the condensation temperature calculated by an iteration procedure;  $p^{\circ} = 1 \text{ Pa}$ . <sup>f</sup> Standard uncertainty in  $p$  was calculated with  $u(p/\text{Pa}) = 0.005 + 0.025(p/\text{Pa})$  for  $p < 5 \text{ Pa}$  and  $u(p/\text{Pa}) = 0.025 + 0.025(p/\text{Pa})$  for  $p > 5$  to  $3000 \text{ Pa}$ .

formation about the synthesis of the TATP used in this work and in literature publications is summarized in Table 3.

In many cases no sufficient data about the details of sample synthesis have been provided, whilst samples that have been recrystallized from methanol were reported with different sublimation characteristics regarding the enthalpy of sublimation at 298.15 K. In this work the crude product was extracted from the reaction mixture with pentane. The data published by Mbah *et al.* [25] for the crude product of synthesis under hydrochloric acid catalysis is in fair agreement with the data obtained in this work. (cf. Table 4, Fig-

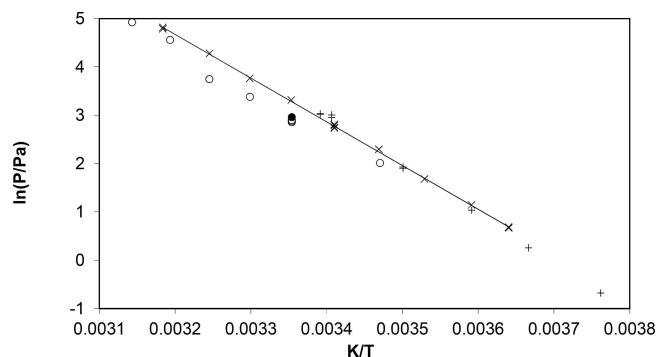
ure 4) For TATP an average uncertainty-weighted value for  $\Delta_{\text{cr}}^{\text{g}} H_m^{\circ}$  (298.15 K) of  $80.8 \pm 0.5 \text{ kJ mol}^{-1}$  is calculated considering all available sets of data. This value is not in agreement with the one obtained in this work ( $76.7 \pm 0.7 \text{ kJ mol}^{-1}$ ), which is supposedly caused by the polymorphism of TATP and different methods of synthesis in all measurements. The vapor pressures of TATP at 298.15 K that were calculated from each individual complete dataset are compiled in Table 4. The mean value of 6.9 Pa is in agreement with the value measured in this work (6.7 Pa).

**Table 3.** Details of TATP synthesis in this work and in literature references.

Experiment <sup>a</sup>	Acid <sup>b</sup>	Solvent	Purity	Melting Point Range °C	$\Delta_{cr}^g H_m^\circ$ (298.15 K) <sup>d</sup> kJ mol <sup>-1</sup>
This Work	H <sub>2</sub> SO <sub>4</sub>	Pentane	99.9% <sup>e</sup>	97–98	76.7 ± 0.7
Mbah 2015 HCl [25]	HCl	–	–	–	71.6 ± 6.9
Mbah 2015 H <sub>2</sub> SO <sub>4</sub> [25]	H <sub>2</sub> SO <sub>4</sub>	–	impure	–	66.6 ± 3.8
Mbah 2014 [27]	–	–	–	86	68.0 ± 6.3
Egorshhev 2013 [30]	HCl	–	–	95–97	98.7 ± 7.7
Rivera 2011 [34]	–	–	–	–	(73.0)
Damour 2010 [31]	CAR <sup>c</sup>	Methanol	–	94.2–95.2	85.7 ± 0.9
Oxley 2010 [28]	H <sub>2</sub> SO <sub>4</sub>	Methanol	“good”	–	92.8 ± 2.7
Oxley 2009 [26a]	–	–	–	–	72.0 ± 3.3
Dunayevskiy 2007 [32]	–	–	–	–	(85.4)
Rivera 2006 [29]	–	–	–	95.9	86.8 ± 2.2
Oxley 2005 [26b]	H <sub>2</sub> SO <sub>4</sub>	Methanol	“good”	–	103.8 ± 6.4

<sup>a</sup> First author and year of publication, <sup>b</sup> Acid catalyst used in synthesis, <sup>c</sup> CAR: Cationic Acid Resin <sup>d</sup> Molar Enthalpy of Sublimation at 298.15 K <sup>e</sup> (VO-GC/MS)

The sublimation behavior of DADP was studied in this work in the temperature range from 274.7–314.1 K. The absolute vapor pressures  $p_{sat}$  and thermodynamic properties of sublimation obtained by the transpiration method in this work for DADP are compiled in Table 2. A comparison of own data with literature experiments regarding the enthalpies of sublimation is compiled in Table 4. Figure 5 shows a *Clausius-Clapeyron* plot of the own and literature p-T data for the sublimation of DADP.



**Figure 5.** Experimental vapor pressure of DADP in comparison with literature values x: this work, + [31], ● [33], ○ [26a] Linear regression line for this work.

Available p-T literature measurement data for comparison are provided by Egorshhev *et al.* [30] (static method), Brady *et al.* [33] (thermogravimetry), Damour *et al.* [31] (Knudsen effusion), and Oxley *et al.* [26a] (headspace). The thermogravimetric analysis measurement by Brady *et al.* [33] is excluded from data comparison and average value calculation since solely a p-T-equation and a vapor pressure extrapolation to 298.15 K was published. For DADP an average uncertainty-weighted value for  $\Delta_{cr}^g H_m^\circ$  (298.15 K) of  $76.4 \pm 0.4$  kJ mol<sup>-1</sup> is recommended considering all available

sets of data. This value is in fair agreement with the one obtained in this work ( $75.0 \pm 0.5$  kJ mol<sup>-1</sup>). The vapor pressures of DADP at 298.15 K that were calculated from each individual complete dataset are compiled in Table 4. The mean value of 25.5 Pa is in fair agreement with the value measured in this work (26.6 Pa).

### 3.5 Estimation of the Air Concentration of Peroxides 1 and 2

Vapor pressures are measured under ideal saturation conditions. In a real case scenario the saturation equilibrium of the explosive will not be reached and diffusion processes will dictate the air concentration of the explosive. Dravnicks *et al.* [35] have stated a mathematical model for the estimation of the non-equilibrium air concentration of an explosive, which shall be applied to TATP and DADP in the following using the equations and values provided by Bird *et al.* [36].

Fick's Law of Diffusion provides a suitable approximation for the rate of molecular vapor emission per cm<sup>2</sup>  $J$ :

$$J = A \times D_{AB} \times \frac{n_c - n_a}{d} \quad (4)$$

$J$ : emission flux [molecules s<sup>-1</sup>],  $A$ : area of explosive exposed to air [cm<sup>2</sup>],  $D_{AB}$ : diffusivity of explosive vapor in air [cm<sup>2</sup>s<sup>-1</sup>],  $n_c$ : concentration of explosive under saturation conditions [molecules cm<sup>-3</sup>],  $n_a$ : concentration of the explosive in air [molecules cm<sup>-3</sup>],  $d$ : thickness of non-turbulent layer air [cm]

The concentration of the explosive in the air is considered to be negligibly small ( $\rightarrow n_a = 0$ ) and the thickness of the non-turbulent layer of air surrounding the explosive is considered to be 0.2 cm [35].

**Table 4.** Compilation of data on the enthalpy of sublimation and vapor pressures obtained in this work and from literature values for TATP and DADP.

Experiment <sup>a</sup>	Method <sup>b</sup>	T-Range K	$T_{avg}$ K	$\Delta_g H_m^\circ(T_{avg})$ kJ mol <sup>-1</sup>	$\Delta_g H_m^\circ(298.15 \text{ K})^c$ kJ mol <sup>-1</sup>	$p_{sat}$ Pa
<b>TATP</b>						
This Work	T	274.3–314.1	294.3	76.9 ± 0.6	76.7 ± 0.7	6.7
Mbah 2015 HCl [25]	H	292.7–327.2	310.3	71.1 ± 6.9	71.6 ± 6.9	7.6
Mbah 2015 H <sub>2</sub> SO <sub>4</sub> [25]	H	292.7–327.2	310.3	66.1 ± 3.7	(66.6 ± 3.8)	(6.5)
Mbah 2014 [27]	G	298.0–327.0	313.2	67.4 ± 6.2	68.0 ± 6.3	(1.9)
Egorshv 2013 [30]	S	348.2–367.2	357.9	96.2 ± 7.6	98.7 ± 7.7	(1.6)
Rivera 2011 [34]	G,O	303.0–338.0	320.5	72.1	(73.0)	-
Damour 2010 [31]	K	269.9–307.0	287.0	86.6 ± 0.8	85.7 ± 0.9	5.9
Oxley 2010 [28]	G	313.9–332.5	321.9	91.7 ± 2.5	92.8 ± 2.7	(24.4)
Oxley 2009 [26a]	H	288.2–323.2	305.0	71.7 ± 3.2	72.0 ± 3.3	8.7
Dunayevskiy 2007 [32]	Q,O	243.2–331.2	285.5	86.0	(85.4)	(6.3)
Rivera 2006 [29]	G	298.2–348.2	319.4	85.8 ± 2.2	86.8 ± 2.2	(2.8)
Oxley 2005 [26b]	H	285.2–331.2	305.3	103.4 ± 6.4	103.8 ± 6.4	5.8
<b>DADP</b>						
This Work	T	274.7–314.1	294.4	75.2 ± 0.4	75.0 ± 0.5	26.6
Egorshv 2013 [30]	S	340.7–393.0	358.5	74.3 ± 1.5	76.6 ± 1.5	25.6
Brady 2012 [33]	G,O	333.2–369.2	351.2	73	(74.8)	(19.3)
Damour 2010 [31]	K	265.9–294.9	284.7	84.6 ± 1.1	84.0 ± 1.2	31.2
Oxley 2009 [26a]	H	288.2–323.2	305.0	79.4 ± 3.4	79.6 ± 3.4	18.6
					76.4 ± 0.4 <sup>e</sup>	25.5 <sup>f</sup>

<sup>a</sup> First author and year of publication, <sup>b</sup> Methods: T: Transpiration, H: Headspace, S: Static Method, G: Thermogravimetric Analysis, K: Knudsen-Effusion, Q: Quantum-Cascade Laser Photoacoustic Spectroscopy, O: Equation Only <sup>c</sup> Enthalpies of vaporization were adjusted according to Chickos *et al.* [24] with the values for  $\Delta_g H_m^\circ$  and  $C_{p,m}^\circ$  (cr) stated in Table 5 <sup>d</sup> Vapor pressure at 298.15 K, calculated according to equation (2). <sup>e</sup> Weighted average value, calculated using the uncertainty as the weighing factor. <sup>f</sup> Average value. Values in brackets were excluded from average value calculation.



**Table 5.** Calculation of Molar Heat Capacity Differences at T = 298.15 K

compound	$C_{p,m}^o$ (l) calc. [J mol <sup>-1</sup> K <sup>-1</sup> ]	$C_{p,m}^o$ (cr) calc. [J mol <sup>-1</sup> K <sup>-1</sup> ]	$C_{p,m}^o$ (l) lit. [J mol <sup>-1</sup> K <sup>-1</sup> ]	$C_{p,m}^o$ (cr) lit. [J mol <sup>-1</sup> K <sup>-1</sup> ]	$\Delta_l^g C_{p,m}^o$ [J mol <sup>-1</sup> K <sup>-1</sup> ]	$\Delta_{cr}^g C_{p,m}^o$ [J mol <sup>-1</sup> K <sup>-1</sup> ]
TATP	379.3 <sup>a</sup>	(314.6) <sup>a</sup>	n.a.	271.8 [22]	-109.2	-41.5
DADP	252.9 <sup>a</sup>	(209.7) <sup>a</sup>	n.a.	223.4 [22]	-76.3	-34.3

Bracketed values not used for calculation of heat capacity differences. n.a.: not available a) calculated according to the increment method and data by Hurst et al. [23] b) calculated by  ${}^gC_{p,m}^o = 10.58 + C_{p,m}^o(l) \times 0.26$  according to [24] c) calculated by  ${}^gC_{p,m}^o = 0.75 + C_{p,m}^o(cr) \times 0.15$  according to [24]

The diffusivity  $D_{AB}$  can be calculated by the following formula:

$$D_{AB} = 0.0018583 \sqrt{T^3 \left( \frac{1}{M_A} + \frac{1}{M_B} \right) \frac{1}{p \sigma_{AB}^2 \Omega_{D,AB}}} \quad (5)$$

$T$ : Temperature [K] (298.15 K),  $M_A$ : Molecular Mass of Explosive [g mol<sup>-1</sup>],  $M_B$ : Molecular Mass of Air [g mol<sup>-1</sup>] (28.97 g mol<sup>-1</sup>),  $p$ : total pressure [atm] (1 atm),  $\sigma_{AB}$ : combined collision diameter [Å],  $\Omega_{D,AB}$ : collision integral for diffusion [ ]

$$\sigma_{AB} = 1/2(\sigma_A + \sigma_B) \quad (6)$$

$\sigma_A$ : collision diameter of explosive [Å],  $\sigma_B$ : collision diameter of air [Å] (3.617 Å) [36]

$$\varepsilon_{AB} = \sqrt{\varepsilon_A \varepsilon_B} \quad (7)$$

$\varepsilon_A$ : characteristic energy of explosive [J],  $\varepsilon_B$ : characteristic energy of air [J]

Whilst the collision diameter of  $\sigma_B$  (3.617 Å) [36] and the characteristic energy  $\varepsilon_B$  ( $\varepsilon_B/\kappa = 97.0$  K) [36] of air is known, the collision diameter of the explosive  $\sigma_A$  and its characteristic energy  $\varepsilon_A$  have to be estimated. These values may be estimated from the solid at the melting point (m):

$$\varepsilon/\kappa = 1.92T_m; \sigma = 1.222^a \sqrt{V_m} \quad (8)$$

$T_m$ : melting point [K],  $V_m$ : volume of the solid at the melting point [cm<sup>3</sup> mol<sup>-1</sup>],  $\kappa$ : Boltzmann's constant (1.38066 × 10<sup>-23</sup> J K<sup>-1</sup>)

With  $\varepsilon_{AB}$  the collision integral for diffusion  $\Omega_{D,AB}$  can be calculated according to:

$$\Omega_{D,AB} = \frac{1.16145}{T^{*0.15610}} + \frac{0.19300}{\exp(476335T^*)} + \frac{1.03587}{\exp(1.52996T^*)} + \frac{1.76474}{\exp(3.89411T^*)} \quad (9)$$

In case of TATP and DADP the diffusion coefficient can be calculated from their melting point (eq. (8)). The needed molar volume  $V_m$  can be approximated from the crystal structure density at the temperature  $T_{XRD}$ : The density can

be adjusted to the melting point by the following equation [37]:

$$T^* = \kappa T / \varepsilon_{AB} \quad (10)$$

$\rho_m$ : density at melting point [g cm<sup>-3</sup>],  $\rho_{XRD}$ : density from X-Ray diffraction [g cm<sup>-3</sup>],  $T_{XRD}$ : temperature of XRD-experiment [K]

$$\rho_m = \rho_{XRD} / (1 + 0.00015(T_m - T_{XRD})) \quad (11)$$

The molar volume at the melting point can be calculated by:

$$V_m = M / \rho_m \quad (12)$$

With equations (4) to (12) the diffusion coefficient of a solid explosive in air can be approximated when solely its melting point and a density are known and equation (4) can be used to calculate the mass flux of material from the explosive to the air with  $A = 1$  cm<sup>2</sup>,  $n_a = 0$  and  $d = 0.2$  cm.

If the concentration  $n_c$  is converted to partial pressure ( $n_c = 3.3 \times 10^{16} p$ ,  $p$ : vapor pressure [Pa]) and the emission flux is converted into a mass flux (unit conversion factor:  $M/N_A$ ) the mass flux can be calculated:

$$Q = \frac{D_{AB}}{0.2 \text{ cm}} \times 3.3 \times 10^{16} \times \left( \frac{760}{101325} \right) p \times (M/N_A) \quad (14)$$

$Q$ : emission flux of explosive [g s<sup>-1</sup> cm<sup>-2</sup>],  $N_A$ : Avogadro Constant (6.022 × 10<sup>23</sup> mol<sup>-1</sup>)

An example of this calculation can be found for TATP 1 and DADP 2 in Table 6:

With the emission flux  $Q$  in hands the concentration of the explosive in air at the diffusion equilibrium state can be calculated:

$$c_{dif} = S \times Q \times r \quad (15)$$

$c$ : concentration of explosive in air at diffusion equilibrium,  $S$ : surface of explosive exposed to air,  $r$ : attenuation factor (10<sup>-4</sup>)

The attenuation factor  $r$  has been established in the study by Dravnicks *et al.* [35]. For a surface of 200 cm<sup>2</sup> the

**Table 6.** Example of calculation for the emission flux of explosive Q for TATP and DADP at STP conditions (298.2 K, 1 atm)

	TATP	DADP	Unit
$T_m$	370.2 <sup>a</sup>	405.2 <sup>a</sup>	K
$\rho_{XRD}$	1.27 <sup>b</sup>	1.33 <sup>b</sup>	g cm <sup>-3</sup>
$T_{XRD}$	180 <sup>b</sup>	208 <sup>b</sup>	K
$\rho_m$	1.24	1.292	g cm <sup>-3</sup>
$M$	222.237	148.158	g mol <sup>-1</sup>
$V_m$	179.981	114.691	cm <sup>3</sup> mol <sup>-1</sup>
$\sigma_A$	6.899	5.937	Å
$\varepsilon_B/K$	710.688	777.888	K
$\sigma_{AB}$	5.258	4.777	Å
$\varepsilon_{AB}/K$	262.558	274.691	K
$\kappa T/\varepsilon_{AB}$	1.136	1.085	
$\Omega_{D,AB}$	1.355	1.385	
$D_{AB}$	0.050	0.062	cm <sup>2</sup> s <sup>-1</sup>
$p_{sat}$	6.7 <sup>a</sup>	26.6 <sup>a</sup>	Pa
$Q$	0.154	0.498	μg cm <sup>-2</sup> s

<sup>a</sup> value obtained in this work, <sup>b</sup> values obtained from the literature for TATP [15] and DADP [16].

following values for  $c_{dif}$  can be obtained: TATP: 3.1 ng L<sup>-1</sup>, DADP: 10 ng L<sup>-1</sup>. These values must be regarded as the maximum concentrations of explosive that can be present for detection since further diffusion barriers like foil wrapped around the explosive are highly probable.  $c_{dif}$  is directly proportional to the exposed surface of the explosive (Equation 15) and was calculated in this work for an exemplary surface of 200 cm<sup>2</sup>.

Using the Ideal gas equation the saturation concentration of an explosive can be calculated:

$$c_{sat} = \frac{p_{sat} \times M}{R \times T} \quad (16)$$

$c_{sat}$ : saturation concentration [mg L<sup>-1</sup>],  $R$ : ideal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>),  $T$ : temperature [K]

For TATP a value of 600 μg L<sup>-1</sup> and for DADP a value of 1589 μg L<sup>-1</sup> can be calculated using the vapor pressures stated in Table. This indicates that the diffusion phenomenon discussed lowers the gas phase concentration of the explosive by about five orders of magnitude (10<sup>5</sup>).

## 4 Conclusions

Based on theoretical predictions using the EXPLO5 v6.03 code, TATP and its side product DADP are considered to be medium performance explosives that are easily accessible from openly available chemicals. Whilst for DADP the p-T-values obtained in this work are in agreement with literature values the p-T-values obtained for TATP are not in

agreement with literature values. This might be due to the rich polymorphism of TATP. It would be recommendable to carry out future vapor pressure measurements of TATP with the synthetic procedure detailed in this work for the reason of comparability. The saturation equilibrium concentrations of TATP (600 μg L<sup>-1</sup>) and DADP (1589 μg L<sup>-1</sup>) are about five magnitudes higher than at the diffusion equilibrium state (1: 3.1 ng L<sup>-1</sup>, 2: 10 ng L<sup>-1</sup>) for a surface of 200 cm<sup>2</sup>. The latter concentrations correspond to a ppt-concentration level and are valuable for the conception of gas phase detection devices.

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## References

- [1] R. Wolffenstein, Über die Einwirkung von Wasserstoffsuperoxyd auf Aceton und Mesityloxyd, *Ber. Dtsch. Chem. Ges.* **1895**, *28*, 2265–2269.
- [2] <http://news.nationalpost.com/news/world/german-police-seize-bomb-firearm-in-raid-that-foiled-imminent-boston-marathon-style-terror-attack>
- [3] <http://www.nydailynews.com/news/world/paris-suicide-bombers-tatp-homemade-explosive-article-1.2435082>
- [4] <http://www.n-tv.de/panorama/17-Jaehriger-hortete-Sprengstoff-article334469.html>
- [5] a) J. C. Oxley, J. L. Smith, L. Steinkamp, G. Zhang, Factors Influencing Triacetone Triperoxide (TATP) and Diacetone Diperoxide (DADP) Formation: Part 2, *Propellants, Explos., Pyrotech.* **2013**, *38*, 841–851; b) J. C. Oxley, J. L. Smith, P. R. Bowden, R. C. Rettinger, Factors Influencing Triacetone Triperoxide (TATP) and Diacetone Diperoxide (DADP) Formation: Part 1, *Propellants, Explos., Pyrotech.* **2013**, *38*, 244–254.
- [6] J. C. Oxley, J. L. Smith, J. E. Brady, L. Steinkamp, Factors Influencing Destruction of Triacetone Triperoxide (TATP), *Propellants, Explos., Pyrotech.* **2014**, *39*, 289–298.
- [7] D. Lubczyk, A. Hahma, M. Brutschy, C. Siering, S. R. Waldvogel, A New Reference Material and Safe Sampling of Terrorists Per-

- oxide Explosives by a Non-Volatile Matrix, *Propellants, Explos., Pyrotech.* **2015**, *40*, 590–594.
- [8] a) R.-M. Räsänen, M. Nousiainen, K. Peräkorpä, M. Sillanpää, L. Polari, O. Anttalainen, M. Utriainen, Determination of gas phase triacetone triperoxide with aspiration ion mobility spectrometry and gas chromatography–mass spectrometry, *Anal. Chim. Acta* **2008**, *623*, 59–65; b) J. L. Anderson, A. A. Cantu, A. W. Chow, P. S. Fussell, R. G. Nuzzo, J. E. Parmeter, G. S. Sayler, J. n. M. Shreeve, R. E. Slusher, M. Story, W. Trogler, V. Venkatasubramanian, L. A. Waller, J. Young, C. F. Zukoski, Existing and Potential Standoff Explosives Detection Techniques, National Academies Press, Washington, DC, **2004**; c) C. L. Rhykerd, D. W. Hannum, D. W. Murray, J. E. Parmeter, Guide for the Selection of Commercial Explosives Detection Systems for Law Enforcement Applications, National Institute of Justice Office of Science and Technology, Washington, DC, **1999**; d) J. Cabalo, R. Sausa, Trace detection of explosives with low vapor emissions by laser surface photofragmentation–fragment detection spectroscopy with an improved ionization probe, *Appl. Opt.* **2005**, *44*, 1084–1091; e) J. I. Steinfeld, J. Wormhoudt, Explosives Detection: A Challenge for Physical Chemistry, *Ann. Rev. Phys. Chem.* **1998**, *49*, 203–232; f) G. Bunte, J. Hürttlen, H. Pontius, K. Hartlieb, H. Krause, Gas phase detection of explosives such as 2,4,6-trinitrotoluene by molecularly imprinted polymers, *Anal. Chim. Acta* **2007**, *591*, 49–56; g) <http://www.sedet.com/Technology.html>
- [9] N. A. Milas, A. Golubovic, Studies in Organic Peroxides. XXVI. Organic Peroxides Derived from Acetone and Hydrogen Peroxide, *J. Am. Chem. Soc.* **1959**, *81*, 6461–6462.
- [10] K. B. Landenberger, O. Bolton, A. J. Matzger, Two Isostructural Explosive Cocrystals with Significantly Different Thermodynamic Stabilities, *Angew. Chem., Int. Ed.* **2013**, *52*, 6468–6471.
- [11] O. Reany, M. Kapon, M. Botoshansky, E. Keinan, Rich Polymorphism in Triacetone-Triperoxide, *Cryst. Growth Des.* **2009**, *9*, 3661–3670.
- [12] C. R. Groom, I. J. Bruno, M. P. Lightfoot, S. C. Ward, The Cambridge Structural Database, *Acta Crystallogr.*, **2016**, *B72*, 171–179.
- [13] Impact: Insensitive > 40 J, less sensitive ≥ 35 J, sensitive ≥ 4 J, very sensitive ≤ 3 J; Friction: Insensitive > 360 N, less sensitive = 360 N, sensitive < 360 N and > 80 N, very sensitive ≤ 80 N, extremely sensitive ≤ 10 N. According to the UN Recommendations on the Transport of Dangerous Goods.
- [14] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision A02, Gaussian, Inc., Wallingford, CT, USA, **2009**.
- [15] F. Dubnikova, R. Kosloff, J. Almog, Y. Zeiri, R. Boese, H. Itzhaky, A. Alt, E. Keinan, Decomposition of triacetone triperoxide is an entropic explosion, *J. Am. Chem. Soc.* **2005**, *127*, 1146–1159.
- [16] F. G. Gelalcha, B. Schulze, P. Lonnecke, 3,3,6,6-Tetramethyl-1,2,4,5-tetroxane: a twinned crystal structure, *Acta Crystallogr.* **2004**, *C60*, o180–o182.
- [17] J. de Zeeuw, S. Reese, J. Cochran, S. Grossman, T. Kane, C. English, Simplifying the setup for vacuum-outlet GC: Using a restriction inside the injection port, *J. Sep. Sci.* **2009**, *32*, 1849–1857.
- [18] N. Haroune, A. Crowson, B. Campbell, Characterisation of triacetone triperoxide (TATP) conformers using LC-NMR, *Sci. Justice* **2011**, *51*, 50–56.
- [19] C. Denekamp, L. Gottlieb, T. Tamiri, A. Tsoglin, R. Shilav, M. Kapon, Two Separable Conformers of TATP and Analogues Exist at Room Temperature, *Org. Lett.* **2005**, *7*, 2461–2464.
- [20] a) V. N. Emel'yanenko, S. P. Verevkin, Benchmark thermodynamic properties of 1,3-propanediol: Comprehensive experimental and theoretical study, *J. Chem. Thermodyn.* **2015**, *85*, 111–119; b) S. P. Verevkin, A. Y. Sazonova, V. N. Emel'yanenko, D. H. Zaitsau, M. A. Varfolomeev, B. N. Solomonov, K. V. Zherikova, Thermochemistry of Halogen-Substituted Methylbenzenes, *J. Chem. Eng. Data* **2015**, *60*, 89–103; c) S. P. Verevkin, Experimental Thermodynamics, Volume 7 (Eds.: R. D. Weir, T. W. D. Loos), Elsevier, **2005**, pp. 5–30.
- [21] E. C. W. Clarke, D. N. Glew, Evaluation of thermodynamic functions from equilibrium constants, *Trans. Faraday Soc.* **1966**, *62*, 539–547.
- [22] R. Pilar, J. Pachman, R. Matyáš, P. Honcová, D. Honc, Comparison of heat capacity of solid explosives by DSC and group contribution methods, *J. Therm. Anal. Calorim.* **2015**, *121*, 683–689.
- [23] J. E. Hurst, B. Keith Harrison, Estimation of Liquid and Solid Heat Capacities Using a Modified Kopp's Rule, *Chem. Eng. Commun.* **1992**, *112*, 21–30.
- [24] W. Acree, J. S. Chickos, Phase Transition Enthalpy Measurements of Organic and Organometallic Compounds. Sublimation, Vaporization and Fusion Enthalpies From 1880 to 2010, *J. Phys. Chem. Ref. Data* **2010**, *39*, 043101.
- [25] J. Mbah, D. Knott, S. Steward, D. Cornett, Vapor Pressure and Sublimation Enthalpy of Triacetone Triperoxide by a Gas Chromatography Headspace Approach, *Int. J. Energ. Mater. Chem. Propul.* **2015**, *14*, 321–329.
- [26] a) J. C. Oxley, J. L. Smith, W. Luo, J. Brady, Determining the Vapor Pressures of Diacetone Diperoxide (DADP) and Hexamethylene Triperoxide Diamine (HMTD), *Propellants, Explos., Pyrotech.* **2009**, *34*, 539–543. b) J. C. Oxley, J. L. Smith, K. Shinde, J. Moran, Determination of the vapor density of triacetone triperoxide (TATP) using a gas chromatography headspace technique, *Propellants, Explos., Pyrotech.* **2005**, *30*, 127–130.
- [27] J. Mbah, D. Knott, S. Steward, Thermogravimetric study of vapor pressure of TATP synthesized without recrystallization, *Talanta* **2014**, *129*, 586–593.
- [28] J. Oxley, J. L. Smith, J. Brady, S. Naik, Determination of Urea Nitrate and Guanidine Nitrate Vapor Pressures by Isothermal Thermogravimetry, *Propellants, Explos., Pyrotech.* **2010**, *35*, 278–283.
- [29] M. L. Ramírez, L. C. Pacheco-Londoño, Á. J. Peña, S. P. Hernández-Rivera, Characterization of peroxide-based explosives by thermal analysis, *Proc. SPIE*, **2006**, *6201*, 62012B1–62012B10.
- [30] V. Y. Egorshv, V. P. Sinditskii, S. P. Smirnov, A comparative study on two explosive acetone peroxides, *Thermochim. Acta* **2013**, *574*, 154–161.
- [31] P. L. Damour, A. Freedman, J. Wormhoudt, Knudsen Effusion Measurement of Organic Peroxide Vapor Pressures, *Propellants, Explos., Pyrotech.* **2010**, *35*, 514–520.

- [32] I. Dunayevskiy, A. Tsekoun, M. Prasanna, R. Go, C. K. N. Patel, High-sensitivity detection of triacetone triperoxide (TATP) and its precursor acetone, *Appl. Opt.* **2007**, *46*, 6397–6404.
- [33] J. E. Brady, J. L. Smith, C. E. Hart, J. Oxley, Estimating Ambient Vapor Pressures of Low Volatility Explosives by Rising-Temperature Thermogravimetry, *Propellants, Explos., Pyrotech.* **2012**, *37*, 215–222.
- [34] H. Félix-Rivera, M. L. Ramírez-Cedeño, R. A. Sánchez-Cuprill, S. P. Hernández-Rivera, Triacetone triperoxide thermogravimetric study of vapor pressure and enthalpy of sublimation in 303–338 K temperature range, *Thermochim. Acta* **2011**, *514*, 37–43.
- [35] A. Dravnicks, R. Brabets, T. A. Stanley, Evaluating Sensitivity Requirements of Explosive Vapor Detector Systems, IIT Research Institute Technology Center, Chicago Illinois, **1972**.
- [36] R. B. Bird, W. E. Stewart, E. N. Lightfoot, Transport Phenomena, Second Edition, John Wiley & Sons, Inc., New York, **2002**.
- [37] C. Xue, J. Sun, B. Kang, Y. Liu, X. Liu, G. Song, Q. Xue, The  $\beta$ - $\delta$ -Phase Transition and Thermal Expansion of Octahydro-1,3,5,7-Tetranitro-1,3,5,7-Tetrazocine, *Propellants, Explos., Pyrotech.* **2010**, *35*, 333–338.
- [38] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist, *Organometallics* **2010**, *29*, 2176–2179.

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