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Triacetone triperoxide thermogravimetric study of vapor pressure and enthalpy of sublimation in 303–338 K temperature range

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ABSTRACT

Vapor pressure measurements are critical for the development and selection of technologies for detection of energetic materials and other hazardous compounds. Peroxide based homemade energetic materials have become of increased interest due to their popular use in improvised explosive devices (IED's) and because they are not easily detected by traditional explosives detection devices. In this work, thermogravimetric analysis was used as a quick and effective assessment method of the vapor pressure and enthalpy of sublimation of acetone peroxide (a cyclic organic peroxide). The results showed an enthalpy of sublimation of 72.1 kJ mol^{-1} which is in good agreement with available literature. Results obtained by thermogravimetry for a series of energetic nitrocompounds were compared to the literature reported values with other methods presenting a relative error of less than 10%. The thermal data obtained in all experiments was used to find relationships between the thermal properties of these compounds and their structural properties. A correlation between enthalpy of sublimation and melting temperature and structural properties (dipole moment, moment of inertia) of the molecules studied was observed.

1. Introduction

1.1. Importance of vapor pressure

Estimation of vapor pressures and enthalpies of sublimation of commercial and homemade energetic materials is useful for the development of trace and vapor-phase detection technologies [1–4] and to understand the environmental fate and transport of these important contaminants [5,6]. Fundamental studies on the sublimation of energetic materials supports applied research of both trace residue and vapor phase detection approaches. A report from the National Research Council addresses how researching the vapor space surrounding a bomber or an improvised device may lead to improved means of detecting energetic materials [4]. At the same, it is important to evaluate the environmental impact of a compound. The transport, volatilization and persistence of a released compound in the principal areas of environmental impact such as water, air and soil can be evaluated and understood by knowing the vapor pressure of the compound at ambient temperatures [5].

1.2. Estimating vapor pressure

A variety of approaches to characterize the vapor pressure of materials have been reported. These methods include direct measurement using a manometer [6], direct monitoring of the gas-phase concentration species [7] and measurements of sample volatilization [8] and vapor pressure and enthalpies of sublimation of organic crystalline compounds [9] by vacuum diffusion (Knudsen cell).

The use of thermal gravimetric analysis (TGA) based methods to characterize the vapor pressure and enthalpies of sublimation and vaporization of volatile materials have also been reported extensively in the literature. Gueckel et al. measured the volatilization rates of pesticides at ambient pressure using isothermal thermogravimetry [10]. In 1998 Price and Hawking proposed a procedure for estimating the vapor pressure and the enthalpy of sublimation by TGA based on the linear relationship between the mass loss rate and the vapor pressure for a thermally stable compound [11]. The mathematical expression that correlates mass loss rate with the vapor pressure derives from Langmuir's work of 1913 [12] given by Eq. (1):

$$\frac{dm}{dt} = P\alpha\sqrt{\frac{M}{2\pi RT}} \qquad (1)$$

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where dm/dt is the mass loss rate (MLR) (kg s^{-1}) at a given temperature provided that the cross sectional area of the sample pan remain constant during the experiment, P is the vapor pressure (Pa), M is the molecular weight of the evaporating compound (kg mol^{-1}), R is the ideal gas constant (J K^{-1} mol^{-1}), T is the absolute temperature (K), and α is the vaporization coefficient. In a vacuum, α is assumed to be 1, but in a flowing-gas atmosphere as in the TGA experiments, α will have different values. Therefore, this term has to be estimated and accounted for real experimental conditions. Rearranging the Langmuir equation gives:

$$P = k\nu \qquad (2)$$

where k is a constant that includes the vaporization coefficient $[\alpha^{-1}(2\pi R)^{1/2}]$ and ν is related to the constant mass loss rate $(dm/dt)(T/M)^{1/2}$. The value for k is independent of a sample and becomes a calibration constant determined from mass loss data of a material with known vapor pressures at experimental temperatures. This expression is then used to estimate the vapor pressure of unknown materials at the same temperatures from the determined mass loss rate data [13].

The methods based on thermogravimetry and Langmuir expression to estimate the vapor pressure have demonstrated to be accurate over a narrow temperature range and for materials with ideal behavior. For these materials the mass loss rate will be constant during isothermal or nearly isothermal conditions. Some groups have used this approach to estimate the vapor pressure of pharmaceutical compounds [14–18]. The applications also include the examination of antioxidants [19], dyes [11] and explosives [20]. Pieterse and Focke [21] and Phang et al. [22] proposed alternate methods considering the molecule diffusion into the gas to treat thermogravimetric data to estimate the vapor pressure of materials that do not present an ideal behavior. However the methods based on the work by Price including the estimation of an evaporation coefficient (α) within k from experimental data at target conditions continue to be widely applied. The results from different studies have demonstrated that the method is a rapid and reliable approach to obtain accurate vapor pressure values.

1.3. *Estimating enthalpy of sublimation*

The enthalpy of sublimation can be obtained from vapor pressure data by means of the Clausius–Clapeyron expression [16,23]. The data for the vapor pressure obtained from Eq. (2) can be fitted into Eq. (3) resulting in a straight-line plot of slope $\Delta H/R$. In a similar approach, the data of dm/dt can be directly fitted to Eq. (3) to obtain the change in enthalpy from the slope.

$$\ln(P) = B - \frac{\Delta H_s}{RT} \qquad (3)$$

This equation relates the vapor pressure P (Pa), enthalpy of sublimation ΔH_s (kJ mol^{-1}) and the absolute temperature T (K). The constants R and B are the ideal gas constant (J mol^{-1} K^{-1}) and the constant specific to a given instrument and set of experimental conditions and procedures but independent of material and temperatures used [16], respectively.

1.4. *Application to energetic materials*

In this study the vapor pressure of a variety of energetic compounds is estimated using the methodology described by Price and Hawkins. The objective of this research was to compare the vapor pressure and enthalpy of sublimation of triacetone triperoxide (TATP) with respect to more known energetic materials like nitrotoluenes and cyclonite (RDX) using a simple thermogravimetric study in the assessment of the reactivity of this material. TATP is a very unstable and powerful homemade energetic material (HME) that can be used both as a primary or secondary explosive. Peroxide-based improvised explosive devices (IED's) have become of increased interest mainly because they are easily prepared and are not detected by conventional methods of explosives detection since they do not contain nitrogen as constituent element. Peroxide based IED's are widely used all over the Middle East, and have recently been used in attacks like the explosion in the mass transportation system in London (2005). In addition, the information obtained by TGA was used in quantitative structure–property relationships (QSPR) to evaluate the structural parameters that induce sublimation and to predict the enthalpy of sublimation of new materials based on their structure.

Table 1
Melting points of the nitrocompounds used in this study.

Material	Melting point (K)
p-Nitroaniline	421
o-Nitroaniline	344
m-Nitroaniline	387
p-Nitroanisole	321
p-Nitrotoluene	326
p-Dinitrobenzene	447
o-Dinitrobenzene	391
4-Nitrobiphenyl	387
2,4,6-Trinitrotoluene	354
2,4-Dinitrotoluene	343
RDX	479
Acetone peroxide	364
Naphthalene	355
Benzoic acid	395

The results indicate that TGA, in isothermal and dynamic modes, can be used as a rapid and useful method for the study of the vapor pressure and the enthalpy of sublimation of energetic materials. The relative error of the method was evaluated by comparing the results for a series of nitrocompounds using this method with available literature values.

2. Experimental

2.1. *Materials*

Table 1 shows the melting points of the nitrocompounds that were used. These materials were acquired from commercial sources. TATP and 1,3,5-trinitro-1,3,5-triazacyclohexane (cyclonite or RDX) were synthesized according to methods reported in the literature [24,25]. Benzoic acid and naphthalene were acquired from Fisher with a purity of 99.6% and 99%, respectively.

2.2. *Methods*

2.2.1. *TG and DSC analysis*

TA Instruments Q10 differential scanning calorimeter (DSC) with an ultra high purity nitrogen gas flow (40 mL min^{-1}) was used for determining melting temperature of the synthesized highly energetic materials. High pressure hermetic pans were used for the DSC experiments. The samples were sealed under a nitrogen flow to maintain an inert atmosphere. For energetic materials it is recommended to use 1–3 mg of sample. A heating rate of 5 K min^{-1} was used for all samples. The DSC was calibrated with respect to temperature and enthalpy with indium (NIST Traceable melting point: 429.75 K). TGA measurements were performed in a TA Instrument Q-500 Thermal Gravimetric Analyzer. All samples were contained within standards aluminum pans (5 mm I.D.) placed on top of the platinum sample holder. A constant nitrogen purge of 60 mL min^{-1} was maintained through the TGA furnace. The TGA was calibrated for temperature using the nickel Curie point (630 K) and for weight according to manufacturer's optimized procedures.

All samples were first evaluated from room temperature (RT) to 773 K at 5 K min^{-1} for a preview of the mass loss profile and material thermal stability. The sublimation study and vapor pressure estimation with TGA consisted of mass loss rate determination at several isothermal points over a temperature range lower than the sample melting point. In order to ensure reproducibility on the data, samples were analyzed three times. The experiments were conducted over a time range that allow constant mass loss measurements and maintain a constant surface area. Instrumental conditions were determined by evaluating the widely accepted vapor pressure standard, benzoic acid [26]. The vapor pressure of the material at selected temperatures was estimated using literature values for the material [8,9]. The calibration constant (k) and the expression for estimating the vapor pressure from mass loss measurements was obtained from linear regression analysis (Equation 2) of benzoic acid vapor pressure vs. ν in the 303–343 K range.

To assure the applicability of proposed data analysis the vapor pressure was estimated on a temperature range lower than the melting transition and where constant mass loss rate was observed with time. Vapor pressure data for the nitrocompounds and TATP were used to estimate the enthalpy of sublimation according to Equation 3. In a similar approach, Equation 3 was used to obtain the enthalpy of sublimation directly from the mass loss rate measurements. All data were compared to literature values when available. This comparison was used to evaluate the expected error in the enthalpies of sublimation of materials evaluated by TG and the values that have not been reported previously.

2.2.2. QSPR analysis

Molecular descriptor generation is a process to obtain several parameters based on the electronic and topologic molecular structure. The structures of all the molecules included in the structure property relationship analysis were optimized using the Gaussian 03$^{\text{TM}}$ chemical computations software package (Gaussian, Inc., Wallingford, CT) [27]. A B3LYP DFT method with 631G** basis set was applied for the structure optimization. In the quantitative structure property relationship (QSPR) study, topological descriptors were derived using PCDM Software$^{\text{TM}}$ (Molecular Descriptor Calculation v. 2.0) and using the Gaussian input file. The quantum descriptors were derived directly from B3LYP optimization of the molecule. All data were analyzed using the statistical analysis computer program SPSS$^{\text{TM}}$ (Statistical Package for the Social Sciences) ver. 17.0 software (SPSS, Inc., Chicago, IL) and Statgraphics Centurion for Windows$^{\text{TM}}$ (StatPoint Technologies, Inc., Warrenton, VA) to find a relationship between the structure and the enthalpy of sublimation.

3. Results and discussion

3.1. TG and DSC analysis

TGA provides information on the mass changes that arise during thermal events and DSC data gives an assessment of the stability of compounds in the thermal range studied. Fig. 1(a) and (b) shows the DSC and TGA data obtained for TNT and TATP, respectively. The heating rate used was 5 K min^{-1}. TNT does not present a considerable mass loss until above 423 K. Since this mass loss occurs after melting, but before the decomposition temperature, it can be assumed that it is associated with vaporization. The boiling point is not observed in the DSC thermogram because the test is performed in a hermetically sealed pan, keeping the sample mass constant. The loss of mass that occurred before the melting transition (356 K) for TATP suggests a high sublimation rate and high vapor pressure, even before the solid–liquid transition. TATP is therefore, a good candidate for thermogravimetric-based sublimation studies due to its constant mass loss at temperatures below decomposition.

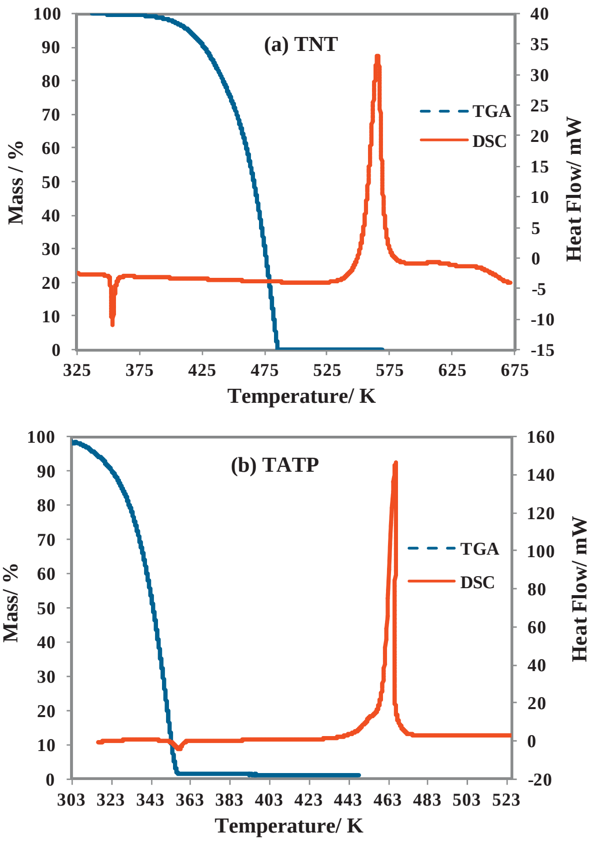

Fig. 1. TGA (left axis) and DSC (right axis) curves: (a) TNT at 5 K min^{-1}. The overlay presents the thermal stability of TNT through heating. The mass loss after 423 K can be associated to vaporization; (b) TATP at 5 K min^{-1}. The high mass loss before melting is associated to the high sublimation and not to decomposition.

The correlation of mass loss rate (ν) vs. vapor pressure for benzoic acid is presented in Fig. 2. The high correlation coefficient ($R^2 > 0.99$) indicates that the experimental conditions are appropriate for the proposed method. The calibration constant, $k = 1.517 \times 10^9$, was determined from the graph. This data was used to estimate the vapor pressure and enthalpy of sublimation of TATP and other materials according to their mass loss rate (ν) and Eq. (2).

Table 2 shows the mass loss rate data (MLR) for TATP. These mass loss rate values were used to estimate the vapor pressure and

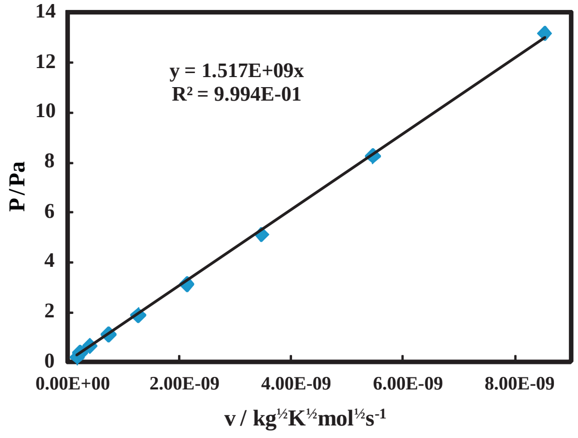

Fig. 2. Vapor pressure calibration using the vapor pressure of benzoic acid and the isothermal mass loss rate from 303.15 to 343.15 K.

Table 2
MLR data for TATP in a temperature range from 303 to 338 K.

Temperature (K)	MLR ($kg\,s^{-1}$)
303	1.15E−10
308	1.93E−10
313	3.09E−10
318	5.00E−10
323	7.87E−10
328	1.16E−09
333	1.56E−09
338	1.99E−09

Table 3
Vapor pressure of some energetic materials at 303 K and 323 K obtained by TG analysis.

Material	P (Pa) @ 303 K experimental	P (Pa) @ 323 K experimental
p-Nitroaniline	0.02	0.05
o-Nitroaniline	0.26	1.89
m-Nitroaniline	0.15	0.31
p-Nitroanisole	0.58	4.29
p-Nitrotoluene	5.11	30.47
p-Dinitrobenzene	0.07	0.23
o-Dinitrobenzene	0.08	0.34
2,4,6-Trinitrotoluene	-	0.04
2,4-Dinitrotoluene	0.08	0.70
TATP	6.46	45.53

-, not available.

enthalpy of sublimation according to Eqs. (2) and (3). The values for the vapor pressure obtained for some energetic materials at 303 K and 323 K are reported in Table 3. The results for the vapor pressure of energetic materials are in good agreement with the volatility of those compounds. For acetone peroxide, the vapor pressure has been reported by Oxley et al. to be 6.95 Pa [7] and 7.87 Pa [28] at ambient conditions using headspace gas chromatography technique. During this study, the obtained vapor pressure is estimated to be ~6.46 Pa, which is close to the reported value. RDX has a very low mass loss rate and it is difficult to estimate the vapor pressure at the low temperatures reported in this table.

The vapor pressure values estimated from mass loss data were used to obtain the Antoine expression for TATP. Fig. 3 correlates the experimental values with the values obtained from the Antoine expression with $A = 10.32$, $B = -237.97$ and $C = 555.04$. The correlation factor (R^2) was 0.998.

The enthalpy of sublimation of TNT and 2,4-DNT and other nitrocompounds have been previously reported. Therefore, they served as standards for confirmation of the accuracy of the results obtained by thermogravimetry. Table 4 lists the sublimation enthalpies obtained from the MLR data in this study. The results were compared to the values reported by Chickos, who compiled sublimation data from over 1200 references from 1910 to 2001 [29]. The relative error of the enthalpy of sublimation by TGA is less than 10%. This error is acceptable considering the variability of the values reported in the literature.

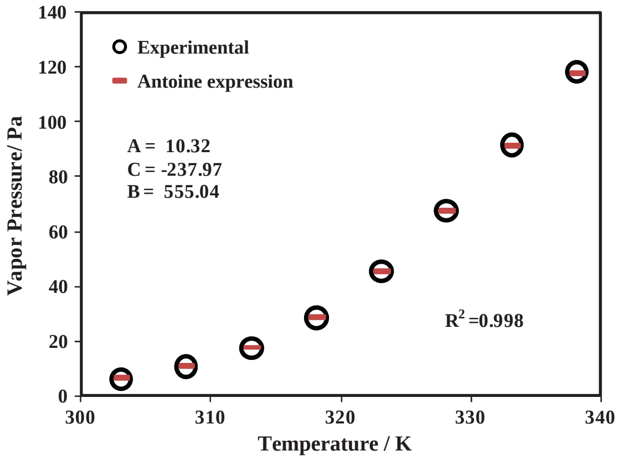

Fig. 3. Antoine correlation for TATP.

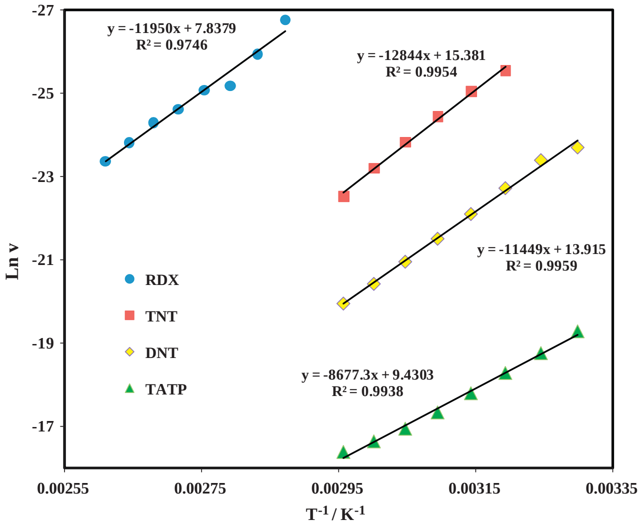

Fig. 4. Curves of the mass loss rate vs. temperature for TATP, RDX, TNT and 2,4-DNT. This plot is used to estimate the enthalpy of sublimation (slope = $-\Delta H/R$).

Table 5 compares the values for the enthalpy of sublimation obtained from Eq. (3) using mass loss rate data instead of P (column 3) with the values obtained from estimated vapor pressure data (column 4). These values were obtained from Eq. (2) as explained in Section 1. These values can be compared with the results compiled by Chickos from studies using other methods (column 5). When the enthalpies of sublimation were obtained from vapor pressure data, the results were closer to the previously reported values than those obtained directly from MLR.

Fig. 4 shows the Clausius–Clapeyron plots ($\ln \nu$ vs. $1/T$) of the well-known explosives RDX, TNT and 2,4-DNT and for the homemade explosive TATP. The enthalpies of sublimation were obtained from the slope of the linear regressions. This method is appropriate for materials that exhibit a high vapor pressure because constant mass loss can be maintained. However, for materials with low vapor pressure, fitting the model is more difficult because of the noise in the data. This was demonstrated by the lower correlation coefficient (R^2) for RDX data. The important nitramine was analyzed at a higher temperature range to induce higher mass loss rates, but this approach can also induce degradation of the material and mass loss due to moisture content loss (data not shown).

In terms of the explosives of interest, literature results for TNT ranged from 102 to 113 $kJ\,mol^{-1}$ and for 2,4-DNT ranged from 95.8 to 98.8 $kJ\,mol^{-1}$. The results for TNT and DNT in this work (106.8 $kJ\,mol^{-1}$ for TNT and 96.2 $kJ\,mol^{-1}$ for 2,4-DNT) are comparable to those presented in the mentioned review article [29]. Only a few references are reported for the sublimation enthalpy of TATP. In 2005, Oxley et al. reported the enthalpy of sublimation of TATP to be 109 $kJ\,mol^{-1}$ by GC–MS [7]. This result is considerably higher than the one found in the current study (72.1 $kJ\,mol^{-1}$). The enthalpy of sublimation was reported to be 85 $kJ\,mol^{-1}$ in a previous study from our group [30] and a very recent study by Oxley et al. reported 73 $kJ\,mol^{-1}$ for the sublimation enthalpy of TATP [28]. Both results are in good agreement with the current results. No recent studies reporting calculations using the vapor pressure of RDX could be found; however, a study from 1969 estimated the

Table 4
Summary of enthalpies of sublimation obtained by TG analysis compared to literature values.

Material	Temperature range experimental (K)	$\Delta_s H$ experimental (kJ mol^{-1})	Temperature range literature (K)	$\Delta_s H$ literature (kJ mol^{-1})	% Relative error from literature
p-Nitroaniline	343–413	98	303–417	101.2 ± 4.0	−3.2
o-Nitroaniline	303–338	87.8	310–319	86.3 ± 4.8	1.7
m-Nitroaniline	323–383	93.6	288–384	95.4 ± 6.7	−1.9
p-Nitroanisole	303–321	91.3	-	-	-
p-Nitrotoluene	303–321	81.3	298–310	79.1	2.8
p-Dinitrobenzene	323–433	88.3	339–398	93.2 ± 3.0	−5.3
o-Dinitrobenzene	323–383	94.0	328–397	86.9 ± 5.4	8.2
4-Nitrobiphenyl	333–380	103.8	-	-	-
2,4,6-Trinitrotoluene	313–338	106.8	293–353	111.2 ± 9.6	−4.0
2,4-Dinitrotoluene	318–338	96.2	277–344	98.3 ± 1.8	−2.1
RDX	348–383	99.5	328–370	130	−23.5
TATP	303–338	72.1	288–323	73	−1.2
Naphthalene	303–348	69.9	250–353	73.9 ± 0.3	−5.4
Benzoic acid	303–343	89.9	298–383	89.7 ± 1.0	0.2

-, Not available.

Table 5
Enthalpy of sublimation results of energetic materials obtained by different methods.

Material	Temperature range experimental (K)	$\Delta_s H$ experimental (kJ mol^{-1}) MLR	$\Delta_s H$ experimental (kJ mol^{-1}) $P = k\nu$	$\Delta_s H$ literature (kJ mol^{-1})
p-Nitroaniline	343–413	96.5	98	101.2 ± 4.0
o-Nitroaniline	303–338	86.5	87.8	86.3 ± 4.8
m-Nitroaniline	323–383	92.2	93.6	95.4 ± 6.7
p-Nitroanisole	303–321	90.0	91.3	–
p-Nitrotoluene	303–321	80.0	81.3	79.1
p-Dinitrobenzene	323–433	86.7	88.3	93.2 ± 3.0
o-Dinitrobenzene	323–383	92.5	94	86.9 ± 5.4
4-Nitrobiphenyl	333–380	102.4	103.8	–
2,4,6-Trinitrotoluene	313–338	105.4	106.8	111.2 ± 9.6
2,4-Dinitrotoluene	318–338	94.9	96.2	98.3 ± 1.8
RDX	348–383	97.8	99.5	130
TATP	303–338	70.8	72.1	73
Naphthalene	303–348	69.7	69.9	73.9 ± 0.3
Benzoic acid	303–343	89.2	89.9	89.7 ± 1.0

enthalpy of sublimation of RDX to be 130 kJ mol^{-1} over 303–345 K [31]. In the present study, that value is reported to be 99.5 kJ mol^{-1} for 338–383 K.

Fig. 5 presents the thermograms for TATP at different heating rates (2, 5 and 10 K min^{-1}). It was possible to estimate the enthalpy of sublimation of the homemade explosive using TG dynamic analysis by applying the same mathematical treatment to the instantaneous mass loss rate in the same temperature range used for isothermal analysis. The enthalpy of sublimation is obtained from the linear regression analysis of temperature and mass loss rate. A value for the enthalpy of sublimation is obtained for each heating rate and the value can be extrapolated to isothermal conditions. Results obtained were 10% different from the isothermal experiments that are accepted as being more accurate.

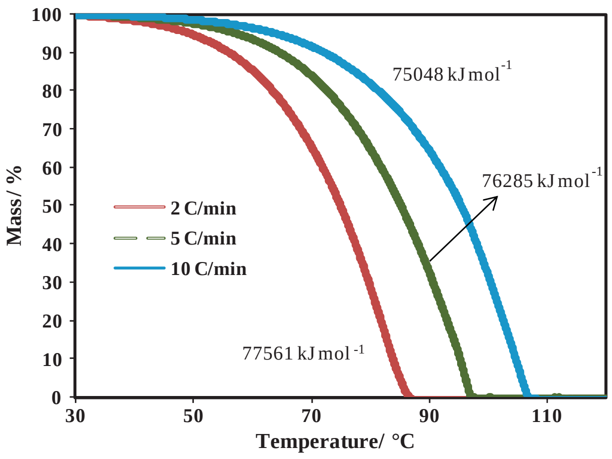

Fig. 5. Determination of enthalpy of sublimation of TATP by dynamic analysis. An extrapolation to heating rate = 0 resulted in an enthalpy of sublimation of 78,050 kJ mol^{-1}.

3.2. QSPR analysis

The thermal data obtained in the experiments were analyzed using a statistical analysis program to find relationships between the thermal properties of these compounds and their structural properties. SPSS Statistics Professional$^{\text{TM}}$ (SPSS, Inc., IBM, Chicago, IL) statistical analysis software program was used to find descriptors with high correlation to the properties. These descriptors were then analyzed by Statgraphics Centurion$^{\text{TM}}$ (v. XVI, StatPoint Technologies, Inc., Warrenton, VA) to find the best fit to a two-variable model. This model was appropriate to predict the enthalpy of sublimation of TATP considering that the data responded to properties of 11 molecules only. Table 6 presents the results of fitting a multiple linear regression model to describe the relationship between thermal properties and the descriptors. When the P-value of the ANOVA test is less than 0.05, there is a statistically significant relationship between the variables at the 95.0% confidence level. The R^2 statistical figure of merit indicates that the model fit explains the percent of the variability in the studied property. The standard error of the estimate shows the standard deviation of the residuals.

Table 6
Structure property relationship results.

Model	R	R^2	Adjusted R^2	Std. error of estimate
(a) SPSS analysis models summary				
1[a]	.657	.431	.375	11.053
2[b]	.796	.634	.553	9.346
3[c]	.931	.868	.818	5.963

Parameter	Estimate	Standard error	T statistics	P-value
(b) Multiple regression results of statgraphics analysis				
Constant	25.217	15.954	1.581	0.153
I	−0.007	0.002	−3.763	0.006
μ	2.333	0.722	3.230	0.012
T_m	0.156	0.042	3.753	0.006

[a] Predictors:(constant), μ.
[b] Predictors:(constant), μ, I.
[c] Predictors:(constant), μ, I, T_m.

This value can be used to understand the prediction limits for new observations. The combination of thermal properties, topological descriptors and quantum descriptors is summarized in Table 6.

A multiple linear regression model was used to describe the sought relationship between the sublimation enthalpy ($\Delta_{sub}H$) and three important molecular properties used as independent variables: melting temperature (K), dipole moment (D) and moment of inertia (kg m^{-2}). The equation of the fitted model was:

$$\Delta_{sub}H = 25.217 - 0.007 \times (I) + 2.333 \times (\mu) + 0.156 \times (T_m) \qquad (4)$$

where I is the moment of inertia, μ is the dipole moment and T_m is the melting temperature. Since the P-value in the ANOVA table (Table 6) is less than 0.05, a statistically significant relationship between the variables at the 95% confidence level was established. Statistical parameters, calculated in the Statgraphics Centurion statistical analysis package, are explained as follows. The simple correlation coefficient R shows a significant relationship between the three variables and the R^2 indicates that the model fit shows results of 86.8% of the variability in the enthalpy. The adjusted R^2 value, which is more suitable for comparing models with different numbers of independent variables, is 81.8%. The standard error of the estimate shows that the standard deviation of the residuals is 5.96 which is a measure of the accuracy of the predictions. Based on the results obtained, the model described on Eq. (4) can be used as a first approach to obtain a good estimation of the enthalpy of sublimation for organic peroxide based highly energetic materials.

4. Conclusions

The characterization and optimization of TGA allowed the estimation of the bulk vapor pressure of compounds and the enthalpy of sublimation from vapor pressure data. The enthalpy of sublimation was also calculated directly from mass loss rate data. A series of nitrocompounds with known enthalpies were analyzed using TGA in this study with differences lower than 10% from the literature values, indicating that TGA can be used as a quick and accurate method to assess the enthalpy of sublimation of improvised formulations of energetic materials. Also, as part of the study thermal analysis was applied to determine the vapor pressure of TATP, a homemade energetic material known for its power, unsteadiness, and attractiveness to terrorists and its impacts on environmental chemistry and compared to the vapor pressure of known energetic compounds such as TNT and RDX. The sublimation rate and enthalpy of TATP was also determined using thermal gravimetric analysis. The enthalpy of sublimation in the temperature range of 303–338 K was estimated using the Clausius–Clapeyron equation as 72.1 kJ mol^{-1}.

The collected data were analyzed seeking for correlations with structural properties of the molecules of the target compounds. Good agreement was obtained for relationships established between the enthalpies of sublimation of the compounds studied and the combined effect of melting temperatures, dipole moments and moments of inertia. However, more data are needed to build more robust models. Future work should include the analysis of more highly energetic materials to further evaluate the models and render them more robust. Then at that stage the models should be able to make predictions on properties of new materials from established correlations between structural data and thermal properties of compounds.

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References

[1] 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. 44 (2005) 1084.
[2] J.I. Steinfeld, J. Wormhoudt, Explosives detection: a challenge for physical chemistry, Annu. Rev. Phys. Chem. 49 (1998) 203.
[3] C.L. Rhykerd, D.W. Hannum, D.W. Murray, J.E. Parmeter, U.S. Department of Justice (Eds.), Guide for the Selection of Commercial Explosives Detection Systems for Law Enforcement Applications, National Institute of Justice, Washington, DC, 1999.
[4] The 9/11 Commission Report: Final Report of the National Commission on Terrorist Attacks Upon the United States, W.W. Norton & Company, New York, 2004.
[5] L. Rittfeldt, Determination of vapor pressure of low-volatility compounds using a method to obtain saturated vapor with coated capillary columns, Anal. Chem. 73 (2001) 2405.
[6] M.J.S. Monte, L.M.N.B.F. Santos, M. Fulem, J.M.S. Fonseca, C.A.D. Sousa, New Static apparatus and vapor pressure of reference materials: naphthalene benzoic acid, benzophenone, and ferrocene, J. Chem. Eng. Data 51 (2006) 386.
[7] J. Oxley, J. Smith, K. Shinde, J. Moran, Determination of the vapor density of triacetone triperoxide (TATP) using a gas chromatography headspace technique, Propellants Explos. Pyrotech. 30 (2005) 127.
[8] M. Colomina, P. Jimenez, C. Turrion, Vapour pressures and enthalpies of sublimation of naphthalene and benzoic acid, J. Chem. Thermodyn. 14 (1982) 779.
[9] M.A.V. Ribeiro da Silva, M.J.S. Monte, L.M.N.B.F. Santos, The design, construction, and testing of a new Knudsen effusion apparatus, J. Chem. Thermodyn. 38 (2006) 778.
[10] W. Gueckel, G. Synnatschke, R. Rittig, A method for determining the volatility of active ingredients used in plant protection, Pestic. Sci. 4 (1973) 137.
[11] D.M. Price, M. Hawkins, Calorimetry of two disperse dyes using thermogravimetry, Thermochim. Acta 315 (1998) 19.
[12] I. Langmuir, The vapor pressure of metallic tungsten, Phys. Rev. 2 (1913) 329.
[13] O.V. Surov, Thermogravimetric method used to determine the saturated vapor pressure in a wide range of values, Russ. J. Appl. Chem. 82 (2009) 42.
[14] J.P. Elder, Sublimation measurements of pharmaceutical compounds by isothermal thermogravimetry, J. Therm. Anal. Calorim. 49 (1997) 897.
[15] S.F. Wright, Determination of the vapor pressure curves of adipic acid and triethanolamine using thermogravimetric analysis, Thermochim. Acta 421 (2004) 25.
[16] M. Xie, T. Ziemba, M. Maurin, Sublimation characterization and vapor pressure estimation of an HIV nonnucleoside reverse transcriptase inhibitor using thermogravimetric analysis, AAPS PharmSciTech. 4 (2003), article 23.
[17] K. Chatterjee, A. Hazra, D. Dollimore, K. Alexander, Estimating vapor pressure curves by thermogravimetry: a rapid and convenient method for characterization of pharmaceuticals, Eur. J. Pharm. Biopharm. 54 (2002) 171.
[18] K. Chatterjee, D. Dollimore, K.S. Alexander, Calculation of vapor pressure curves for hydroxy benzoic acid derivatives using thermogravimetry, Thermochim. Acta 392 (2002) 107.
[19] P. Phang, D. Dollimore, The calculation of the vapor pressures of antioxidants over a range of temperatures using thermogravimetry, Thermochim. Acta 367 (2001) 263.
[20] D.E.G. Jones, P.D. Lightfoot, R.C. Fouchard, Q.S.M. Kwok, Thermal properties of DMNB, a detection agent for explosives, Thermochim. Acta 388 (2002) 159.

[21] N. Pieterse, W.W. Focke, Diffusion-controlled evaporation through a stagnant gas: estimating low vapour pressure from thermogravimetric data, Thermochim. Acta 406 (2003) 191–198.

[22] P. Phang, D. Dollimore, S.J. Evans, A comparative method for developing vapor pressure curves based on evaporation data obtained from a simultaneous TG-DTA unit, Thermochim. Acta 392–393 (2002) 119–125.

[23] I.N. Levine, Physical Chemistry, fifth ed., McGraw-Hill Higher Education, New York, 2002, pp. 213–217.

[24] L.C. Pacheco-Londono, A.J. Pena, O.M. Primera-Pedrozo, S.P. Hernandez-Rivera, N. Mina, R. Garcia, R.T. Chamberlain, R.T. Lareau, An experimental and theoretical study of the synthesis and vibrational spectroscopy of triacetone triperoxide (TATP), Proc. SPIE 5403 (2004) 279.

[25] R. Infante-Castillo, S.P Hernandez-Rivera, Theoretical and experimental vibrational and NMR studies of RDX, Proceedings of the SPIE 6201 (2006) 1–8 (62012F).

[26] R. Sabbah, A. Xu-wu, J.S. Chickos, M.L. Planas Leitao, M.V. Roux, L.A. Torres, Reference materials for calorimetry and differential thermal analysis, Thermochim. Acta 331 (1999) 93.

[27] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, T. Vreven Jr., K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision B.04, Gaussian Inc., Pittsburgh, PA, 2003.

[28] 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. 34 (2009) 539.

[29] J.S. Chickos, J.W.E. Acree, Enthalpies of sublimation of organic and organometallic compounds, J. Phys. Chem. Ref. Data 31 (2002) 537.

[30] M.L. Ramírez, L.C. Pacheco-Londoño, A.J. Peña, S.P. Hernández-Rivera, Characterization of peroxide-based explosives by thermal analysis, Proc. SPIE 6201 (2006), 62012B-10A.

[31] J.M. Rosen, C.J. Dickinson, Vapor pressure and heats of sublimation of some high melting organic explosives, Chem. Eng. Data 14 (1969) 120.