Talanta 87 (2011) 290–294

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Thermo-optical determination of vapor pressures of TNT and RDX nanofilms

Walid M. Hikal*, Jeffrey T. Paden, Brandon L. Weeks

Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409, USA

ARTICLE INFO

Article history:
Received 14 September 2011
Received in revised form 11 October 2011
Accepted 13 October 2011
Available online 20 October 2011

Keywords:
Vapor pressure
Explosives
Sublimation rates
Activation energy
UV-absorbance spectroscopy

ABSTRACT

Accurate thermodynamic parameters of thin films of explosives are important for understanding their behavior in the nanometer scale as well as in standoff detection. Using UV-absorbance spectroscopy technique, accurate thermodynamic parameters such as activation energies of sublimation, sublimation rates, and vapor pressures of the explosives cyclotrimethylenetrinitramine (RDX) and 2,4,6-trinitrotoluene (TNT) were determined. The values of these parameters are in excellent agreement with those reported using traditional experiments based on gravimetry. In terms of the Clapeyron equation, the dependence of RDX and TNT vapor pressures on temperature can be described by the relations $\text{Ln}P\,(\text{Pa}) = 39.6 - 15459/T\,(\text{K})$ and $\text{Ln}P\,(\text{Pa}) = 34.9 - 12058/T\,(\text{K})$, respectively. Heats of sublimation of RDX and TNT were also determined to be 128 kJ/mol and 100.2 kJ/mol, respectively.

1. Introduction

Detection of explosives has recently become an important and extensively investigated issue due to the global rise in terrorist activity [1]. Accurate measurements of the thermodynamic parameters of explosives are crucial for their trace detection. Measurement of the thermodynamic parameters of an explosive in the nanometer scale could be used to determine its persistence. An important consideration in detection of explosives is their vapor signature [2]. Different techniques have been previously used in determining vapor pressure of explosives either directly such as Knudsen effusion and gas saturation methods [3–5] or indirectly such as chromotographic and thermogravimetry analysis (TGA) methods [2,6]. TGA is the most widely used technique in determining thermodynamic parameters in the bulk solid form of explosives and is often calibrated to determine their vapor pressures.

Quartz crystal microbalance (QCM) and atomic force microscopy (AFM) are the only techniques that have been reported to be able to determine activation energy of sublimation and sublimation rates of thin films of explosives in the nanometer/micrometer scale [7–10]. With the aid of modeling, vapor pressure of 2,4,6-trinitrotoluene has been estimated with an uncertainty of ~20% by means of QCM [7]. The use of AFM to determine vapor pressures of energetic materials has not been reported in literature. In addition, the sublimation rates of pentaerythritol tetranitrate (PETN) calculated using AFM are ~30–40 orders of magnitude larger than those determined by TGA [10] which is caused by the errors induced by evaluating the volume and height of the sample. This suggests the inability of AFM to be used to determine/estimate the vapor pressure of low volatile explosives, even with better model development.

Recently, we have reported a new method to determine the sublimation rates of continuous thin films of materials using UV-absorbance spectroscopy [11]. The determined sublimation rates were shown to be more accurate than those obtained using both AFM and QCM.

In using UV-absorbance spectroscopy, the sublimation rate per unit area of a material is given by:

$$\frac{dm}{Sdt} = \frac{\rho}{\alpha}\frac{dA}{dt} = f\exp\left(-\frac{E_a}{K_B T}\right) \qquad (1)$$

where S is the rate of mass loss, S is the surface area, ρ is the density of the material, α is the absorption coefficient, f is the frequency factor, E_a is the activation energy of sublimation, K_B is Boltzmann's constant, and dA/dt is the rate of absorbance change. Thus, in using UV-absorbance spectroscopy, the sublimation rate is given by $\rho dA/\alpha dt$, and a plot of $Ln\,((\rho/\alpha)(dA/dt))$ versus the inverse of absolute temperature yields a straight line following the Arrhenius equation with a slope of $-(E_\alpha/K_B)$ from which the activation energy of sublimation could be calculated.

The accuracy of calculating sublimation rates using UV-absorbance spectroscopy method originates from the elimination of the surface area from the sublimation rate equation which introduces errors to the measured values of the sublimation rates due to the expected large surface roughness, and cracks existing on the surface of a sample.

---

* Corresponding author.
E-mail address: walid.hikal@ttu.edu (W.M. Hikal).

0039-9140/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2011.10.020

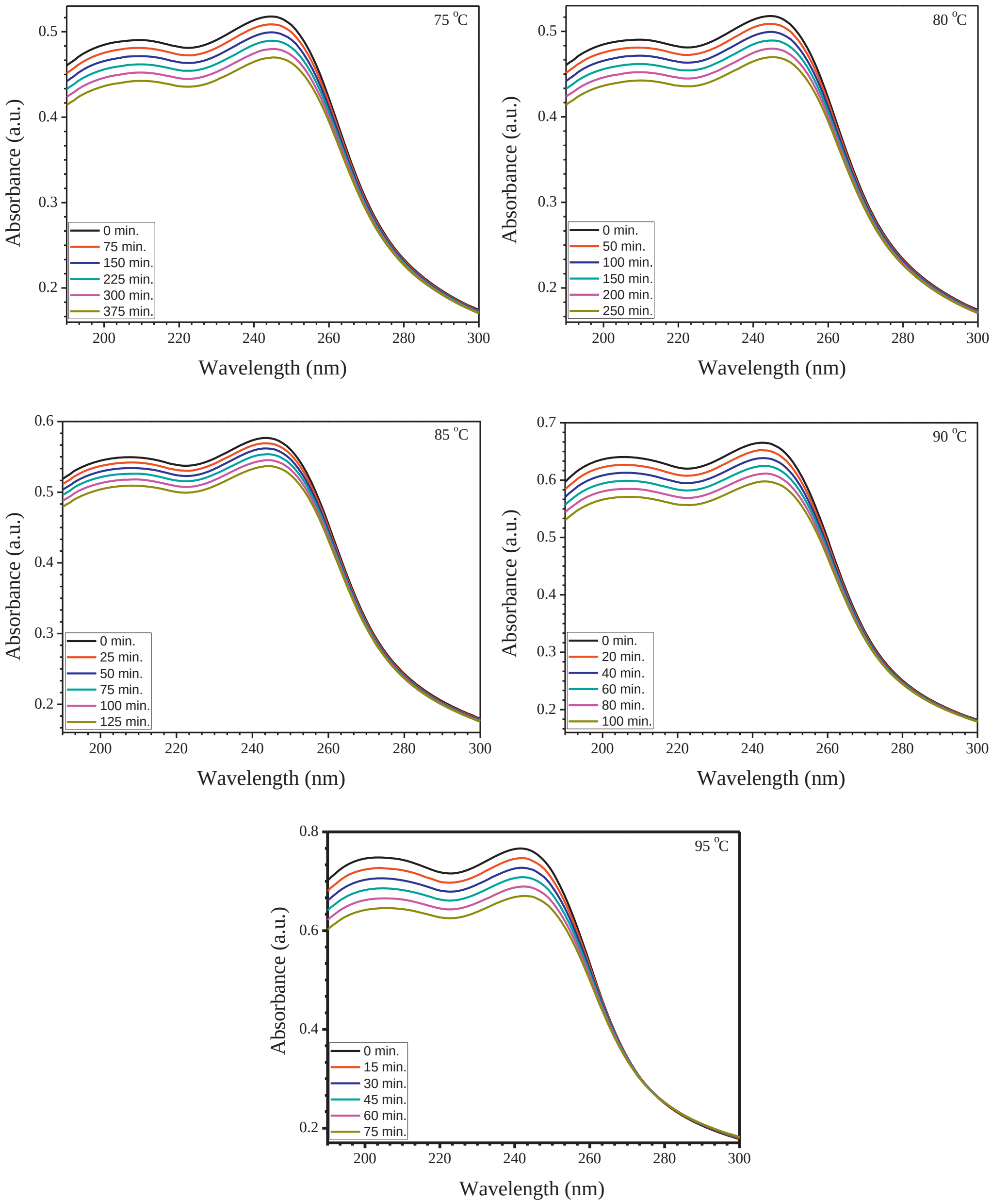

Fig. 1. Isothermal time-dependent change in absorbance spectra of RDX (notice the difference in recording time in the legend).

Starting from Langmuir equation for free evaporation/sublimation, the vapor pressure of any volatile material can be determined [12]. Using a standard material of a well-characterized vapor pressure, a calibration procedure could be used to estimate the vapor pressure of other materials to a good accuracy [13]. For vapor pressure determination, the Langmuir equation is usually written in the form [14]:

$$P = kv \tag{2}$$

where

$$v = \frac{1}{S}\frac{dm}{dt}\sqrt{\frac{T}{M}} \text{ and } k = \frac{\sqrt{2\pi R}}{\alpha}$$

where $(1/S)(dm/dt)$ (kg s^{-1} m^{-2}) is the rate of mass loss per unit area, T is the absolute temperature (K), M is the molecular weight (kg mol^{-1}), R is the universal gas constant (J K^{-1}), and α is the unitless instrument-dependent evaporation constant.

We have also shown the possibility of calibrating a UV spectrometer to determine the vapor pressures of materials. The calculated vapor pressure values were shown to be in excellent agreement with the most accurate and widely used Knudsen effusion method with the advantage of measuring such physical property at relatively lower temperatures.

RDX and TNT are two of the most widely used secondary explosives. They are widely used in detonators, main charges boosters, and plastic explosives [15]. Accurate measurements of thin films of these explosives are of interest for both trace detection and understanding of their behavior in the nanometer/micrometer scale. In this article we report, for the first time, accurate values of thermodynamic parameters, including vapor pressure, of nanofilms of RDX and TNT using UV-absorbance spectroscopy.

2. Materials and methods

RDX powder of high purity was supplied by Sandia National Laboratory and used without further purification. TNT (Austin

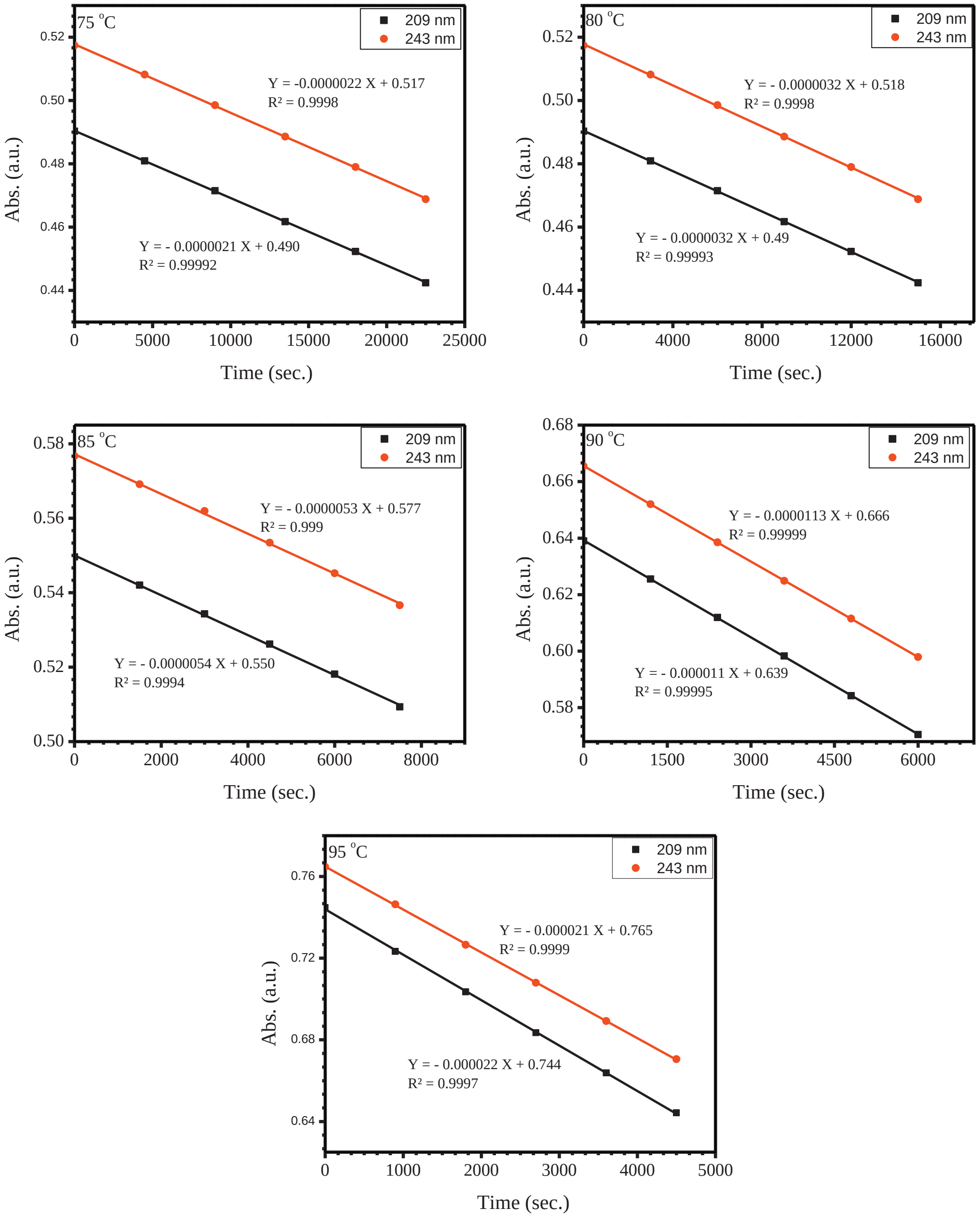

Fig. 2. The temperature-dependent decrease of absorbance of RDX versus time monitored at 243 nm and 209 nm absorbance peaks (notice the different scales).

explosives, Austin, TX) was purified by crystallization of TNT by means of ultrasonication in 2-isopropanol. Both materials were then dissolved in HPLC grade acetone. A stock solution of 0.2 M of both explosives in acetone were used to prepare continuous thin films on quartz substrates by spin coating (single wafer spin processor, Laurell technologies corp., North Wales, PA) 20 μL of each material solution at 3000 rpm for 1 min. The quartz substrates were cleaned using acetone and de-ionized water before films were deposited. Concentrations below 0.2 M were not used since they were found to form non-continuous films.

The thickness and roughness of the thin films were determined using a PSIA XE Atomic force microscope (AFM) (Santa Clara, CA) in contact mode with a silicon cantilever (nanosensor pointprobes, nominal spring constant 5.0 N/m). Absorbance spectra of thin films were recorded *in situ* at different temperatures using a Lambda 1050 UV/Vis/NIR (Perkin–Elmer, UK) spectrometer at 0.5 nm resolution with quartz as reference in the 190–300 nm range. The spectrometer is equipped with a temperature controller allowing for *in situ* temperature-dependent absorbance measurements with an accuracy of 0.05 °C for both sample and reference. All absorbance spectra were collected within 1 h of preparation. The effect of the surface energy between quartz and thin films on the sublimation rate is negligible [8]. The absorbance coefficient of TNT and RDX were calculated using Lambert's law ($A = \alpha L$), where A is the absorbance at a specific wavelength and L is the thickness of the film.

3. Results and discussion

3.1. RDX

Optical images of the RDX films show that the films are continuous and have a faceted shape suggesting they are crystalline. The AFM images of RDX films confirm they are continuous

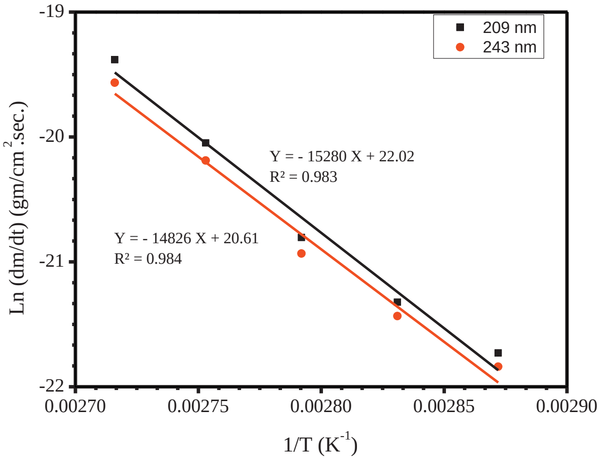

Fig. 3. Log the rate of mass loss versus inverse of absolute temperature in Kelvin monitored at 243 nm and 209 nm absorbance peaks of RDX.

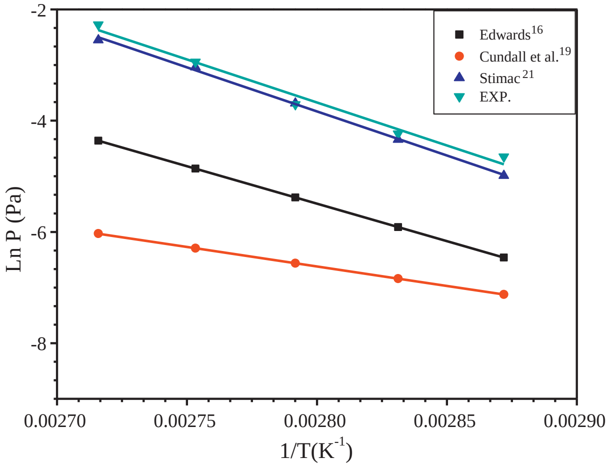

Fig. 4. A plot of the log of the vapor pressure of RDX obtained using UV-absorbance spectroscopy along with those reported in literature.

with thickness of ~500 nm and RMS roughness of ~40 nm. The absorbance spectrum of RDX thin films exhibits two well-defined but relatively broad peaks centered at 349 nm and 309 nm. For accuracy purpose as well as ensuring a homogeneous thickness of the films, the absorbance of three different spots on three different RDX films at room temperature were collected and the average value was used in calculating the absorbance coefficients of the 349 nm and 309 nm peaks. The absorbance coefficients of the 349 nm and 309 nm peaks were determined to be 12,000 cm^{-1} and 10,600 cm^{-1}, respectively. Monitoring the absorbance while quickly increasing/ramping the film temperature, no significant absorbance change was observed indicating that the absorbance coefficients are temperature-independent. No change in absorbance location of the two absorbance peaks was observed during the course of the experiment. In addition, no peak broadening was observed in increasing the RDX films temperature which could further suggest their crystalline nature since peak broadening is an indication of a crystallization behavior.

Due to the extremely low temperature-dependent sublimation rates of RDX which translates into long experiment run time, different films were used at different temperatures. Using different films at different temperatures does not affect the results and no sample to sample normalization is required since we are monitoring absorbance change not absorbance values.

Fig. 1 shows the isothermal time-dependent absorbance spectra of RDX films. It is clear that the decrease in absorbance is temperature-dependent. In addition, Fig. 1 shows a systematic decrease in absorbance with time indicating different sublimation rates of RDX at different temperatures. A plot of the absorbance versus time at different temperatures shown in Fig. 2, indicates that the isothermal time-dependence decrease of the absorbance is linear for both absorbance peaks at all the temperatures used in this study with very good *R* values. The slopes of the best fits in Fig. 2 were used to calculate the rate of mass loss/sublimation rate at each temperature. The logarithms of the sublimation rates at different temperatures monitored at 243 nm and 209 nm absorbance peaks are plotted versus the inverse of temperature in Kelvin and shown in Fig. 3. As evidenced from Fig. 3 the plots yield straight lines for both the 243 nm and 209 nm peaks. Using these lines, the activation energy of sublimation was calculated to be 127 ± 7 kJ/mol and 123.3 ± 6 kJ/mol, respectively. The agreement of these two values indicates the possibility of accurately using a single wavelength to calculate thermodynamic properties of explosives using UV-absorbance spectroscopy. There is a large discrepancy in the value of the activation energy of sublimation of RDX in literature (107–134 kJ/mol) [16–20]. Our value(s) is in a very good agreement with those reported by Edwards [16], Cundall et al. [19], Eiceman et al. [20].

The UV spectrometer was calibrated using benzoic acid as a baseline material since it is the most widely used material in calibrating TGA. Using Eq. (2), the calibration constant of the UV spectrometer was calculated to be $k = 2.09 \times 10^7$. Using this value along with Eq. (2), the vapor pressures of RDX at different temperatures (70–90 °C) were calculated. Fig. 4 (green line) shows the plot of the logarithm of vapor pressures of RDX obtained using UV-absorbance spectroscopy in *Pascal* versus the inverse of the absolute temperature. A few reported measurements on RDX vapor pressure using various techniques were found in literature [16,19,21]. These values were extrapolated to the same temperature range used in this study and plotted in Fig. 4 along with our values. Our data is in excellent agreement with the values reported by Stimac [21] using gravimetry and ion mobility spectrometry and are less than one order of magnitude of the values reported by Edwards [16] using Knudsen effusion methods. This indicates the high accuracy of our reported values of vapor pressures of RDX and their compatibility with those obtained using the most accurate and widely used methods.

3.2. TNT

The activation energy and sublimation rates of TNT determined using UV-absorbance spectroscopy have been previously reported [11]. Results are in agreement with activation energy of sublimation and sublimation rates values reported in literature using QCM [7] and Knudsen effusion methods [22].

As with RDX, the same calibration constant ($k = 2.09 \times 10^7$) of the UV spectrometer was used, along with Eq. (2), to determine the vapor pressures of TNT. Unlike RDX, vapor pressure of TNT has been extensively studied using both direct and indirect vapor pressure determining techniques [6,22–24]. Fig. 5 (dark blue line) shows the plot of the logarithm of vapor pressure of TNT obtained using UV-absorbance spectroscopy in *Pascal* versus the inverse of the absolute temperature. The different reported measurements on TNT vapor pressure were extrapolated to the same temperature range used in this study and plotted along with our results in Fig. 5. The figure shows that the plot is linear with a very good *R* value. It is also clear that our data are in excellent agreement with those reported by Lenchitz and Velicky [22] by means of Knudsen effusion method and Pella [23] by means of electron-capture gas-chromatographic method, not only in the vapor pressures values

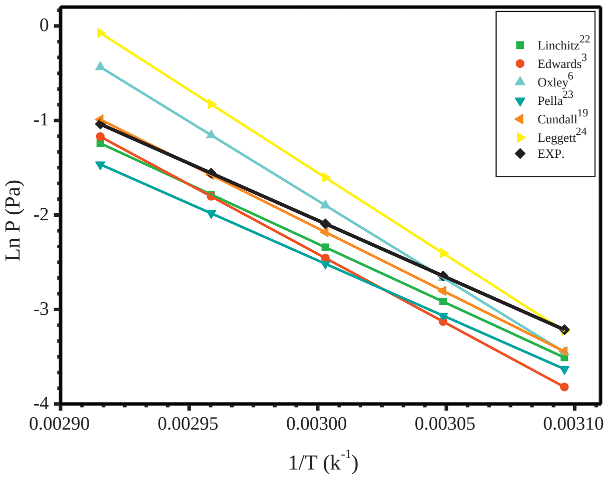

Fig. 5. A plot of the log of vapor pressure of TNT obtained using UV-absorbance spectroscopy along with those reported in literature.

but also in the activation energy of sublimation and sublimation rates of TNT. This indicates the high efficiency of this simple method and the accuracy of our reported thermodynamic parameters. It is also obvious from the data shown in Fig. 5 that the discrepancy of the vapor pressure values of TNT in literature increases with increasing temperature as a result of the expected dissociation of materials at temperatures closer to their melting points. In addition, it is also clear that vapor pressure values reported here using UV-absorbance spectroscopy at the higher temperatures are close to the mean value of those reported in literature. This indicates the accuracy as well as the efficiency of this new method at relatively low temperatures, since some techniques can only determine the values of vapor pressure at high temperature where dissociation of the materials is expected and in turn relatively large values of vapor pressure will be obtained. The foregoing results indicate the accuracy of our reported results and the high potential of this newly developed method to be a dominant technique for determination of vapor pressure of thin films of explosives in the nanometer scale with a high potential for applications in explosives detection as well as their identification as it is based on a unique signature of each explosive.

4. Conclusion

The vapor pressures of nanofilms of two secondary explosives, RDX and TNT, were determined using UV-absorbance spectroscopy. The vapor pressure values of RDX and TNT are in excellent agreement with the values reported in literature using Knudsen effusion and ion mobility methods. We present the first thermodynamic parameters of RDX and TNT in the nanometer scale. We have shown that this simple method is very accurate with efficiency comparable to the most accurate and widely used techniques for determination of less than one Pascal vapor pressures. The data indicate the high potential for use of UV-absorbance spectroscopy in determining vapor pressure of explosives in the nanometer scale. However, this method can be extended to measure thermodynamic parameters of samples in the micrometer scale as long as transparent films can be developed and light transmission through the sample can occur.

Acknowledgment

This work was supported by NSF CAREER (CBET-0644832) and the Office of Naval Research under project number N00014-06-1-0922.

References

[1] M.B. Pushkarsky, I.G. Dunayevskiy, M. Prasanna, A.G. Tsekoun, R. Go, C.K.N. Patel, Proc. Natl. Acad. Sci. U. S. A. 103 (2006) 19630.
[2] J.C. Oxley, J.L. Smith, W. Luo, J. Brady, Propell. Explos. Pyrotech. 34 (2009) 539–543.
[3] G. Edwards, Trans. Faraday Soc. 46 (1950) 423–427.
[4] M.J.S. Monte, L.M.N.B.F. Santos, M. Fulem, J.M.S. Fonseca, C.A.D. Sousa, J. Chem. Eng. Data 51 (2006) 757–766.
[5] M.A.V. Ribeiro da Silva, M.J.S. Monte, L.M.N.B.F. Santos, J. Chem. Thermodyn. 38 (2006) 778–787.
[6] J.C. Oxley, J.L. Smith, K. Shinde, J. Moran, Propell. Explos. Pyrotech. 30 (2005) 127–130.
[7] A.P. Gershanik, Y. Zeiri, J. Phys. Chem. A 114 (2010) 12403–12410.
[8] R. Mu, A. Ueda, Y.C. Liu, M. Wu, M.D.O. Henderson, R.T. Lareau, R.T. Chamberlain, Surf. Sci. 530 (2003) L293–L296.
[9] R. Pitchimani, A.K. Burnham, B.L. Weeks, J. Phys. Chem. B 111 (2007) 9182–9185.
[10] A.K. Burnham, S.R. Qiu, R. Pitchimani, B.L. Weeks, J. Appl. Phys. 105 (2009) 104312.
[11] W.M. Hikal, B.L. Weeks, J. Thermodyn. Anal. (2011), doi:10.1007/s10973-011-1888-8.
[12] I. Langmuir, Phys. Rev. 2 (1913) 329–342.
[13] D.M. Price, 2000. Proceeding of the Twenty-Eight Conference of the North American Thermal Analysis Society, Orlando, FL.
[14] D.M. Price, Thermochem. Acta 367–368 (2001) 253–262.
[15] J. Yinon, Toxicity and metabolism of explosives, CRC Press, Inc. Ann Arbor, 1990, pp. 145–162.
[16] G. Edwards, Trans. Faraday Soc. 49 (1953) 152–154.
[17] J.H. Rosen, C. Dickenson, J. Chem. Eng. Data 14 (1969) 120–124.
[18] J.N. Maycock, V.R. Pai Venecker, Thermochim. Acta 1 (1970) 191–198.
[19] R. Cundall, T.F. Palmer, C.E.C. Wood, J. Chem. Soc. Faraday Trans. 74 (1978) 1339–1945.
[20] G.A. Eiceman, D. Peterson, G. Tiano, J. Rodrigues, J.E. Parameter, Talanta 45 (1997) 57–74.
[21] R. Stimac data published in G.A. Eiceman, D. Preston, G. Tiano, J. Rodrigues, J.E. Parmeter, Talanta 45 (1997) 57–74.
[22] C. Lenchitz, R.W. Velicky, J. Chem. Eng. Data 15 (1970) 401–403.
[23] P.E. Pella, J. Chem. Thermodyn. 9 (1977) 301–305.
[24] D.C. Leggett, J. Chromatogr. 133 (1977) 83–90.