Determination of sublimation rate of 2,4,6-trinitrotoluene (TNT) nano thin films using UV-absorbance spectroscopy

Walid M. Hikal · Brandon L. Weeks

Abstract We report the in situ measurements of the sublimation rate and activation energy of continuous nanofilms of 2,4,6-trinitrotoluene (TNT) in air using UV absorbance spectroscopy. The films were prepared using acetone-dissolved TNT by simple spin coating deposition technique. Unlike traditional mass loss techniques, this new method is independent of the surface area of the sample which contributes to errors in determining physical parameters accurately in both bulk and thin films of materials. The calculated activation energy and temperature-dependent sublimation rates agree well with the reported values for TNT thin films. The results suggest that UV absorbance spectroscopy is an efficient tool in measuring thermodynamic properties in the nanometer scale for materials with absorbance in the UV region of the electromagnetic spectrum.

Keywords 2,4,6-trinitrotoluene · Sublimation rates · Activation energy · UV spectroscopy · Spin coating · Explosives detection

Introduction

Accurate measurements of lifetime of explosives are crucial for their detection. Measurement of the thermodynamic parameters of an explosive in the nanoscale could be used to determine its persistence. Thermogravimetry analysis (TG) is the most widely used technique in measuring sublimation rates of different materials. TG often requires a flow of gas through both the balance chamber and the sample to prevent temperature and pressure build-up [1–3]. However, the mass change detectable by TG is in the order of few nanograms, thereby limiting the usefulness to samples larger than a few milligrams, depending on the sensitivity of the balance. This makes TG an inaccurate technique to study thermodynamic properties of thin films. Quartz crystal microbalance (QCM) is a more sensitive tool for mass loss and has also been used in measuring sublimation rates in thin films [4, 5]. Some materials mass loss could be in the order of attograms. However, QCM sensitivity to mass loss is also in the order of few nanograms with uncertainty of about 15–20%. Atomic force microscopy (AFM) has also been used to determine sublimation rates of thin nanoislands of explosives [6, 7]. However, even when operated with special tips in contact mode, the measurement of the volume and surface area of the films (nanoislands) will lack accuracy. Furthermore, the foregoing techniques lack the ability to discriminate among different materials.

The calculation of the surface area of a sample introduces errors in measuring the sublimation rate of any material in all discussed techniques. The origin of this error is the roughness of the surface. Surface roughness could vary from hundreds of microns to a few microns for single crystals and microcrystalline powders or thin films, respectively. Dislocations as well as cracks that could result in heating a material are also expected to contribute to the errors associated with the calculation of the surface area. In addition, the surface area of the sample is usually measured before performing the experiment and is considered to be constant throughout the experiment. Thus, the calculated sublimation rates per unit area are expected to be smaller than the actual ones.

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Using UV absorbance spectroscopy in determining sublimation rates has the advantage of eliminating the surface area from the rate of mass loss equation. In addition, most importantly, the relatively small scanned area ensures extremely accurate measurements even with the existence of surface roughness, dislocations, and cracks: the surface is relatively smooth within the beam area.
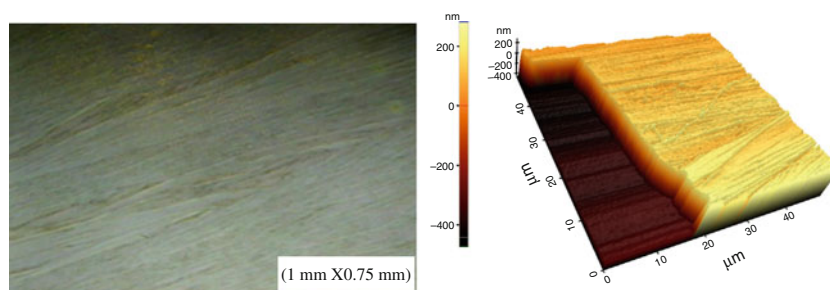
In this report, for the first time, we report our in situ experimental results on using UV absorbance spectroscopy in determining the sublimation rates of the nitroaromatic explosive 2,4,6,-trinitrotoluene (TNT), in the form of continuous thin films, at various temperatures. This is the first technique to measure such parameters based on a unique property of materials absorbing in the UV region with the ability to discriminate among such materials.

Experimental methods

TNT (Austin explosives) was purified by crystallization of TNT by means of ultrasonication in 2-isopropanol. TNT was then dissolved in acetone at room temperature. A stock solution of 0.2 M TNT was used to prepare continuous thin films on quartz substrates by spin coating (single wafer spin processor, Laurell technologies corp., North Wales, PA) 20 µL TNT solutions at 4500 rpm for 1 min. The quartz substrates were cleaned using acetone and de-ionized water before films were deposited. Below 0.2 M concentration, TNT tends to form noncontinuous microparticles/microislands.

The thin films were characterized using 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 nanofilms of TNT were recorded in situ at different temperatures using a Lambda 1050 UV/Vis/NIR (Perkin-Elmer, UK) spectrometer at 0.5 nm resolution and 2 nm slit width with quartz as a reference. The spectrometer is equipped with a temperature controller allowing for in situ temperature-dependent absorbance measurements with an accuracy of 0.05 °C. All absorbance spectra were collected within 1 h of thin films preparation.

Results and discussion

A typical (1×0.75 mm) optical micrograph of a TNT thin film is displayed in Fig. 1a showing that the film is continuous. The continuity of the film is confirmed by a (50×50 µm) AFM image shown in Fig. 1b. The thickness of the films was measured using AFM operated in contact mode at room temperature by removing a part of the film using a tape. As shown in Fig. 1b, the films thicknesses are ~ 500–600 nm with a RMS surface roughness of ~ 30 nm.

The rate of mass loss per unit area due to sublimation/evaporation from a sample of volume V and surface area S at temperature T in Kelvin is given by Arrhenius relation in the form [6, 7]:

$$\frac{\mathrm{d}m}{S\mathrm{d}t} = \frac{\rho \mathrm{d}V}{S\mathrm{d}t} = f \exp\left(-\frac{E_a}{K_B T}\right) \tag{1}$$

where ρ is the density of the material, f is the frequency factor, E_a is the activation energy of sublimation, and K_B is Boltzmann's constant.

Considering a homogeneous sublimation of the material from the surface, hence for a thin film of thickness l and surface area S, Eq. 1 takes the form:

$$\frac{\rho \mathrm{d}l}{\mathrm{d}t} = f \exp\left(-\frac{E_a}{KT}\right) \tag{2}$$

The absorbance (A) of a thin film with thickness l and absorbance coefficient α is given by the Lambert law and can be written as [8, 9].

$$A = \alpha l \tag{3}$$

Differentiating Eq. 3 and substituting in Eq. 2 gives:

$$\frac{\rho}{\alpha} \frac{\mathrm{d}A}{\mathrm{d}t} = f \exp\left(-\frac{E_a}{K_B T}\right) \tag{4}$$

Thus, in using UV spectroscopy, the sublimation rate is given by $\frac{\rho \mathrm{d}A}{\alpha \mathrm{d}t}$, and a plot of $\mathrm{Ln}\left(\frac{\rho}{\alpha}\frac{\mathrm{d}A}{\mathrm{d}t}\right)$ versus the inverse of temperature in Kelvin yields a straight line with a slope of $-\frac{E_a}{K_B}$.

TNT ($\rho = 1.654$ g/cm^3) does not absorb in the visible region of the spectrum and has been reported to exhibit a

Fig. 1 Optical micrograph of TNT thin film (*left*) and AFM image of TNT thin film (*right*) showing the thickness and roughness

(1 mm X0.75 mm)

single peak at 233–235 nm when dissolved in water [10]. TNT thin films exhibit two relatively broad absorbance peaks centered at 264 and 230 nm, in agreement with those values reported for TNT solution in acetone using diffusive reflection [11]. The location of the absorbance peaks was determined from the second derivatives of the absorbance spectra using UV Winlab Data Processor and Viewer software. TNT crystallizes in the form of yellowish thin needles which is not suitable for obtaining a UV absorbance spectrum for comparison application.

To determine the absorbance coefficient of TNT thin films, five samples were prepared and five absorbance spectra were recorded at different spots on each film at room temperature. The absorbance coefficient of the 264 nm peak was found to be 6100 ± 200 cm^{-1}. The dependence of the absorbance coefficient on temperature was monitored while recording the absorbance spectra of TNT thin films at temperatures between 50 and 70 °C. No significant change in absorbance, within the temperature range used in this study, was observed indicating that the
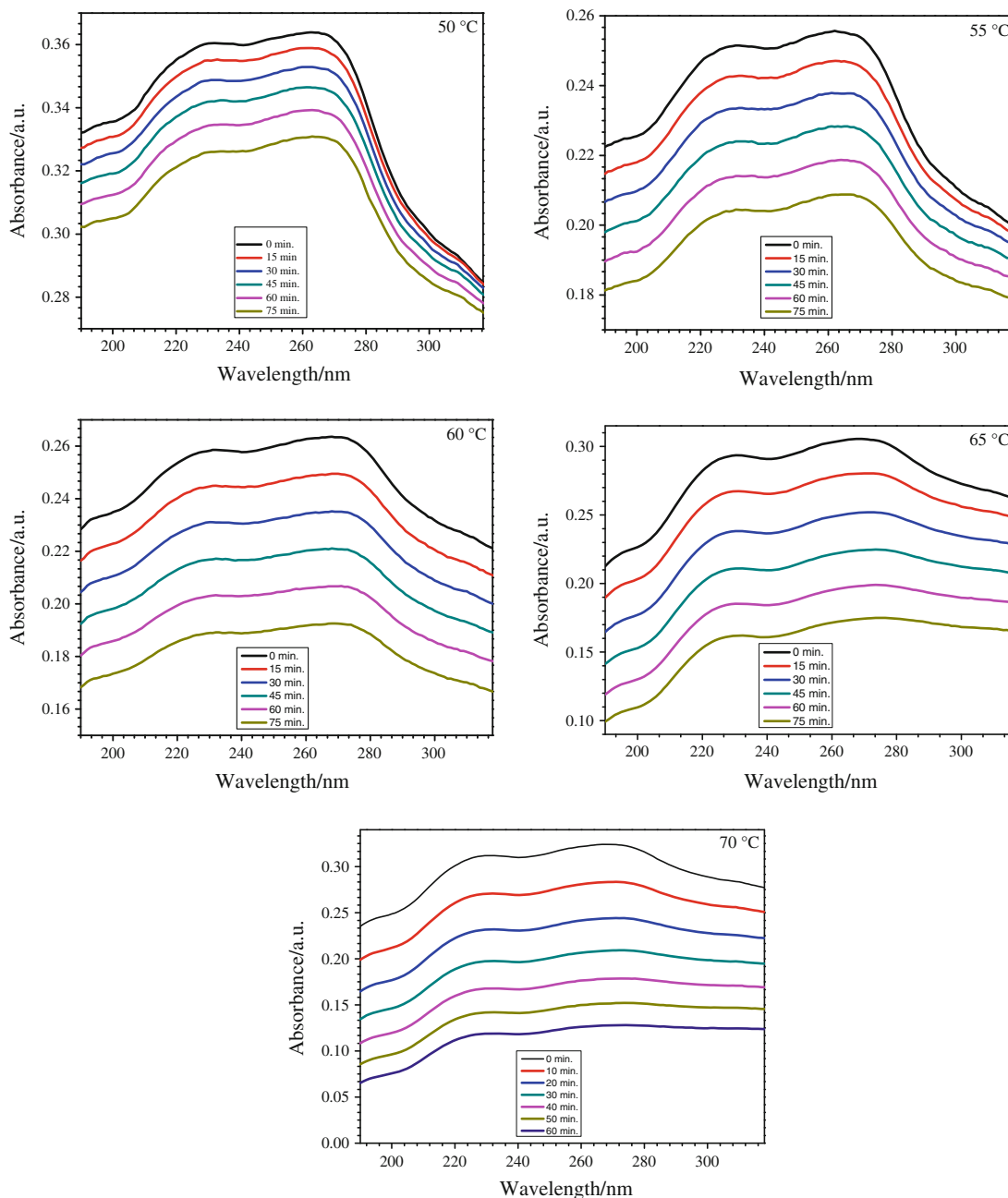

Fig. 2 Time-dependent change in absorbance spectra of TNT at different temperatures (50, 55, 60, 65, and 70 °C)

absorbance coefficient is independent of temperature. However, a broadening in the absorbance spectra evolves with increasing the temperature of those thin films. This broadening is clearly observed, in the spectra shown in Fig. 2, with increasing the temperature of the films. The second derivatives of these spectra indicate that this broadening does not change the location of the absorbance peaks. At lower temperatures, 45 °C and below, the absorbance spectra showed unstable behavior (fluctuations): changes were not as consistent as those observed at higher temperatures. A similar behavior was reported when measuring the sublimation rate of TNT at 45 °C with TG

[12]. The authors suggested that this is due to the low mass loss rate. However, our results at higher temperatures and the sensitivity of the UV spectroscopy technique to the film thickness suggest that detection of such low mass loss (less than one nanometer thickness) with high accuracy is expected. This observation could be due to crystallization or changes in the thickness of the film resulting from diffusion or migration of TNT molecules within the surface of the film due to the relatively high roughness of the surface of the TNT thin films.

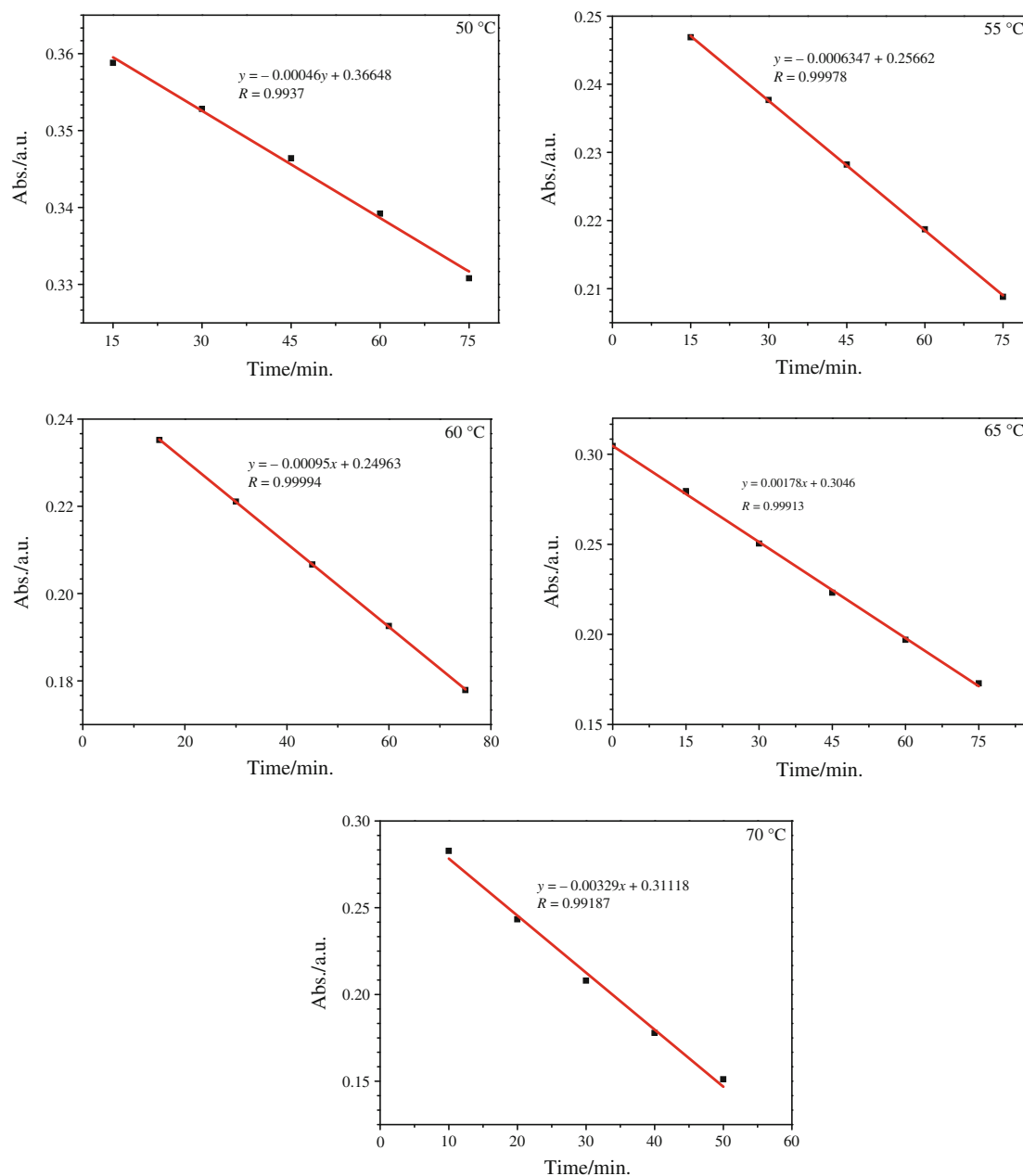Figure 2 shows the change in absorbance spectra of TNT thin films with time at different temperatures (50, 55,

Fig. 3 Isothermal time-dependent absorbance change of TNT (*notice the different scales*). Slope is related to sublimation rate
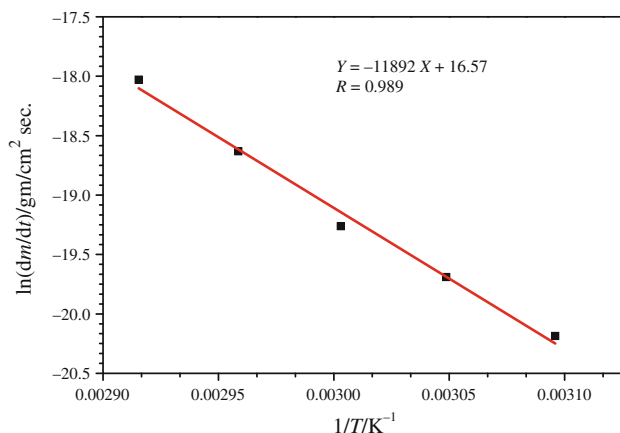
$$Y = -11892\,X + 16.57$$
$$R = 0.989$$

Fig. 4 A plot of the log of the rate of mass loss versus the inverse of temperature in Kelvin. Slope is the activation energy of sublimation (E_a) divided by Boltzmann's constant K_B

60, 65, and 70 °C). The change in absorbance spectra was monitored at the 264 nm peak. However, it is clear that the entire region between 264 and 230 nm in the absorbance spectra is decreased by the same value. It is obvious that the absorbance decreases consistently with time for all temperatures used in this study indicating a systematic temperature-dependent thickness decrease due to sublimation of TNT molecules. The effect of the surface energy between quartz and TNT on the thermodynamic parameters of TNT is considerable only in the range of a few nanometers [5]. Thus, this effect is negligible in our study.

Figure 3 shows that the time-dependence decrease of the absorbance is linear for all temperatures used in this study with very good R values. The slopes of the straight lines in Fig. 3 were used to calculate the rate of mass loss/sublimation rate at each temperature. The logarithm of sublimation rates at different temperatures are plotted versus the inverse of temperature in Kelvin. As shown in Fig. 4, a plot of the log of the rate of mass loss, at different temperatures, versus $1/T$ yields a straight line, from which the heat of sublimation was calculated to be 99.6 ± 5 kJ/mol.

There is a large discrepancy in the activation energy value of TNT in the literature (90–141 kJ/mol) [4, 5, 13–19]. Our value is in a very good agreement with the reported results using the most sensitive techniques used in measuring sublimation rate of TNT: QCM and Knudsen effusion method 97 ± 7 and 103 kJ/mol, respectively [4, 18]. However, a larger value of 131 kJ/mol has been reported using QCM [5]. Interestingly, the calculated sublimation rates are 10–20% higher than those calculated at high temperatures with TG and dimple slide techniques [10] which strongly supports our argument. However, the activation energy reported using these techniques varies between 111 and 132 kJ/mol.

The entropy of the measurement system estimated by the intercept in Fig. 4 is 16.57 kJ/mol. This value is less than those reported in the literature [12]. The results imply that UV absorbance spectroscopy technique is a reliable and accurate technique for measuring thermodynamic properties of materials exhibiting characteristic absorption bands in the UV region in the optical spectrum.

Conclusions

For the first time, we demonstrated that UV spectroscopy is a very powerful technique that can be used to determine thermodynamic properties of continuous thin films of materials with absorbance signature in the UV region. This technique eliminates the errors associated with calculating the surface area and volume of a sample which significantly contributes to errors in calculating thermodynamic properties. The accuracy of the technique is expected to be greater for materials with high absorbance coefficient. This study should also have a direct impact on explosive trace detection device applications due to the high sensitivity (nanometer) to the thickness of the sample. Further investigation on the possibility to use UV absorbance spectroscopy in determining the vapor pressure of materials is being conducted and will be reported.

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