

Determination of Urea Nitrate and Guanidine Nitrate Vapor Pressures by Isothermal

Thermogravimetry

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Abstract:

Since the bombing of Pan Am Flight 103 over Lockerbie, Scotland in 1988, detection of military explosives has received much attention. Only in the last few years has detection of improvised explosives become a priority. To detect these explosives the particulate or vapor must be available. Elsewhere we have reported the vapor pressures of peroxide explosives triacetone triperoxide (TATP), diacetone diperoxide (DADP), and 2,4,6-trinitrotoluene (TNT). Herein we examine the vapor signatures of the nitrate salts of urea and guanidine (UN and GN respectively), and compare them to ammonium nitrate (AN) and TATP using an isothermal thermogravimetric method. The vapor signatures of the nitrate salts are assumed to be the vapor pressures of the neutral parent base and nitric acid. Studies were performed at elevated temperatures [80 to 120°C for UN, 205 to 225°C for GN, 100 to 160°C for AN and 40 to 59°C for TATP], enthalpies of sublimation calculated and vapor pressures extrapolated to room temperature. Reported vapor pressure values (in torr) are as follows:

$$\begin{array}{ccccccc} \text{GN} & \ll & \text{UN} & < & \text{AN} & \ll & \text{TATP} \\ 4.6 \times 10^{-14} & & 6.6 \times 10^{-7} & & 4.3 \times 10^{-6} & & 1.1 \times 10^{-1} \end{array}$$

Keywords: urea nitrate, guanidine nitrate, ammonium nitrate, vapor pressure, energetic salts

Introduction:

Chemical detection of explosives requires a detection signature produced by vapor or particulates. Vapor pressure is a strong indicator of the potential for detection. For most solids, including most explosives, vapor pressures are exceedingly low at ambient temperature, making direct determinations difficult or impossible. While modern explosive detectors claim to be able to detect vapors directly under ambient conditions they are limited in their ability to quantify the information even under controlled experimental conditions. A widely used laboratory approach to obtain ambient vapor pressures is to take advantage of increased vapor pressures with elevated temperature. The temperatures and vapor pressures can then be fitted to the Clapeyron Equation allowing for extrapolation of vapor pressures at other temperatures. Good linearity for this equation implies that the heat of sublimation is relatively constant over the temperature range. Our laboratory has used this approach to obtain estimates of the ambient vapor pressures of 2,4,6-trinitrotoluene (TNT), triacetone triperoxide (TATP), diacetone diperoxide (DADP) and hexamethylene triperoxide diamine (HMTD).^{1,2} For these studies detection and quantification of headspace vapors was accomplished using gas chromatography with electron capture detection. Energetic salts, such as urea nitrate (UN) and guanidine nitrate (GN), generate difficult to detect products with such low volatility that quantification is not possible at ambient temperature. An alternative approach, thermal gravimetric analysis (TGA), was used in this study to obtain sublimation rates at different temperatures which were correlated to a vapor pressure calibration standard, benzoic acid. The TGA method for determining of vapor pressure is well documented and used extensively for evaluations in the pharmaceutical and cosmetic industries.³⁻⁸ In addition to UN and GN, ambient vapor pressures of ammonium nitrate (AN) and TATP were obtained by the TGA method. The chemical structures of UN, GN, AN, and TATP are given in Figure 1.

Comparisons with ambient vapor pressures of AN and TATP, obtained by other methods from the literature, were used to validate the TGA method.

Materials and Methods:

Urea Nitrate (98% purity) was purchased from TCI America. Guanidine nitrate (reagent grade) was obtained from Fluka Chemika. Reagent grades of benzoic acid and ammonium nitrate were acquired from Fisher Scientific. The reference material, triacetone triperoxide (TATP), was synthesized in our laboratory.¹ Mass loss determinations were carried out using a TA Instruments Model SDT 2690 Thermal Gravimetric Analyzer (TGA). A constant nitrogen gas purge (80 mL/min) was used during the experiments. Samples were analyzed in open aluminum pans purchased from TA Instruments. AN, UN and GN samples were kept under vacuum to avoid moisture until used for TGA analysis. The TATP remained at -10°C until use.

The TGA furnace was heated to the desired temperatures and maintained for 10 minutes with nitrogen purge to flush the furnace space. An empty sample pan was tarred in the temperature equilibrated furnace prior to addition of the sample. The pan was quickly removed and the sample added (3 to 10 mg depending on the sample) and promptly returned to the furnace to avoid significant temperature change. Runs were done in duplicate or triplicate at the specified temperatures.

The Antoine equation was used to relate vapor pressure to mass loss per time (i.e. $\mu\text{g}/\text{min}$).⁹⁻¹¹ Benzoic acid, with verified vapor pressures via TGA and other methods, was used as reference material to calibrate the TGA for vapor pressure determinations of the other samples by isothermal thermogravimetry.

Results and Discussion:

Benzoic acid, whose vapor pressure at different temperatures is well documented,^{9,10} is used extensively for such calibrations. The TGA instrument expresses sublimation rate as change in weight percent with time (in minutes). Table 1 includes the instrument calibration data for benzoic acid. Vapor pressures of benzoic acid at the specified temperatures were obtained using the Antoine coefficients in the NIST (<http://webbook.nist.gov>). Figure 2 is a plot of natural logarithm of benzoic acid vapor pressures versus natural logarithm of the sublimation rate in $\mu\text{g}/\text{min}$. The slope and intercept of Figure 2 yields the two pseudo Antoine constants (A and B) for the experimental conditions used in this study according to the Equation (1):

$$\ln P = A \ln \left(\frac{dm}{dt} \right) + B \quad (1)$$

where dm/dt is the experimentally determined sublimation rate in $\mu\text{g}/\text{min}$ and P is the vapor pressure. Based on these results the Antoine constants are $A = 1.327$ and $B = 0.137$, as obtained in Figure 2 and shown in Equation (2).

$$\ln P = 1.327 \ln \left(\frac{dm}{dt} \right) + 0.137 \quad (2)$$

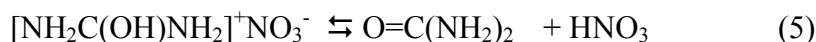
Vapor pressures of AN, UN, GN, and TATP were obtained using Antoine constants determined above from the above and experimentally determined sublimation rates, at specified temperatures. Figures 3 and 4 are representative thermographs of UN and GN percent mass loss with time. The sublimation rates and calculated vapor pressures, at specified temperatures, from Equation 2, are given in Tables 2-5. Using these vapor pressures, at specified temperatures, it is

possible to use the Clapeyron equation to construct graphs of the dependence of vapor pressure on temperature.^{1,2,13} These plots are shown for AN, UN, GN and TATP in Figure 5.

AN and TATP, whose vapor pressures have been determined by other methods, were selected for this study to confirm the validity of the TGA method. The TGA method provides vapor pressure but gives no indication of the composition of the vapor. Like UN and GN, AN is also an energetic salt with a significant vapor pressure at elevated temperature. Ammonium nitrate vaporizes by dissociation above its melting point according to equation (3).¹²



By analogy a similar dissociation mechanism for vaporizations of guanidine nitrate and urea nitrate (equations 4 and 5, respectively) are suggested.



These mechanisms are highly speculative, especially for the ambient conditions. Urea decomposes at its melting point (132°C) and guanidine has a very low melting point (50°C). Other mechanisms and further decompositions are possible. Lack of neutral guanidine or urea in the vapor does not necessarily limit vapor detection to alert for UN or GN. In bulk detection of the explosive TNT, it has a very low vapor pressure and if confined is highly immobile. Contaminating di-nitro-toluene (DNT) has much higher vapor pressure, is highly mobile, relatively easy to detect and alerts to the probable presence of TNT. Likewise, other vapor products traceable to UN or GN could be used in detection. This study provides evidence for the existence of a vapor associated with these compounds albeit the specific composition of the vapor is not known.

The Clapeyron equations, illustrated in Figure 5, describe temperature dependence of the vapor pressures for the four energetic materials studied. They are as follows:

$$\text{For UN} \quad \text{LnP(Pa)} = 57.377 - 20131/T \quad (6)$$

$$\text{For GN} \quad \text{LnP(Pa)} = 72.189 - 33589/T \quad (7)$$

$$\text{For AN} \quad \text{LnP(Pa)} = 35.141 - 12690/T \quad (8)$$

$$\text{For TATP} \quad \text{LnP(Pa)} = 40.194 - 11026/T \quad (9)$$

Given that the slopes of the above Clapeyron equations are enthalpies of sublimation (ΔH_{sub}) divided by the gas constant (R), it is possible to calculate ΔH_{sub} . Enthalpies of sublimation and vapor pressures extrapolated to 25°C from the corresponding Clapeyron equation are given in Table 6. The vapor pressure of TATP, extrapolated to 25°C from its Clapeyron equations (Equations 9), was determined to be 24.8 Pa (0.186 Torr) for TATP. We have previously determined the vapor pressure of TATP at 25°C using a gas chromatography/head space method to be 0.0521 torr.¹ Using the TGA method vapor pressures of TATP are within the range of that reported in the literature. Brandner et al have reported vapor pressures of solid ammonium nitrate in the temperature range of 76-165°C.¹⁸ Using their experimentally determined Clapeyron equation, the extrapolated vapor pressure of AN at 25°C would be 11.1×10^{-6} torr. They used a method of transpiration involving the collection specifically of ammonia and nitric acid (see equation 1) by flowing dry air or nitrogen over 10 to 20 grams of ammonium nitrate. The current study using, TGA, reports a lower vapor pressure of 4.49×10^{-6} torr when calculated from our Clapeyron equation (equation 8).

In conclusion enthalpies of sublimation and vapor pressures extrapolated to 25°C from the corresponding Clapeyron equations for the three energetic salts (UN, AN, GN) and TATP are

given in Table 6. In previous studies we have extensively used quantification of headspace vapors by gas chromatography for solid explosives, such as TNT, with relatively low vapor pressures.^{1,2,13} This has the advantage of identifying the vapor composition by chromatography. Due to exceedingly low vapor pressures we had been unable to use this approach for energetic salts such as AN, UN and GN. The TGA method used in this study can be used for solids with extremely low vapor pressures where gas chromatography is not practical. It was limited in that it provided no information on the composition of the vapor.

References

1. J. C. Oxley, J. L. Smith, K. P. Shinde, J.S. Moran, Determination of the Vapor Density of Triacetone Triperoxide (TATP) Using a Gas Chromatography Headspace Technique, *J. Propellants, Explos., Pyrotech.* **2005**, 30, 2.
2. J.C. Oxley, J.L. Smith, W.Wei, J. Brady, Determining the Vapor Pressures of Diacetone Diperoxide (DADP) and Hexamethylene Triperoxide Diamine (HMTD), *Propellants, Explos., Pyrotech.*, in press.
3. P. Aggarwal, D. Dollimore, K.S. Alexander, The use of Thermogravimetry to follow the Rate of evaporation of an ingredient used in perfumes, *J. Therm. Anal.* **1997**, 49, 595.
4. B. Cassel, Determining Vapor Pressure by Pressure DSC, *Perkin Elmer Thermal Analysis Newsletter.* **1993**, 49, 2.
5. M. Casserino, D.R. Belvins, R.N. Sanders, An Improved Method for Measuring Vapor Pressure by DSC with Automated Pressure Control, *Thermochim Acta.* **1996**, 284, 145.
6. K. Chatterjee, D. Dollimore, K. S. Alexander, A. Hazra, Estimating Vapor Pressure Curves by Thermogravimetry : a Rapid and Convenient method for Characterization of Pharmaceuticals, *Eur. J. Pharm. Biopharm.* **2002**, 54, 171.
7. J. W. Goodrum, E. M. Siesel, Thermogravimetric Analysis for Boiling Points and Vapor Pressure, *J. Thermal Anal.* **1996**, 44, 1251.
8. H. G. Wiedemann, Applications of Thermogravimetry for Vapor Pressure Determination. *Thermochimica Acta*, **1972**, 3, 355.
9. K. Chatterjee, D. Dollimore, K. S. Alexander, A new application for Antonie equation in formulation development, *Int J Pharm.* **2001**, 213, 31.

10. J. P. Elder, Sublimation Measurements of Pharmaceutical Compounds by Isothermal Thermogravimetry, *J. Thermal Anal.* **1997**, 49, 897.
11. M. Xie, T.M. Ziembra, M.B. Maurin, Sublimation characterization and Vapor Pressure Estimation of an HIV Nonnucleoside Reverse Transcriptase Inhibitor using Thermogravimetric Analysis, *AAPS Phram Sci Tech.* **2003**, 4 (2), Article 23.
12. K.R. Brower, J.C. Oxley, M.P. Tewari, Homolytic Decomposition of Ammonium Nitrate at High Temperature, *J. Phy. Chem.* **1989**, 93, 4029.
13. D. C Leggett, Vapor Pressure of 2, 4, 6- Trinitrotoluene by a Gas Chromatographic Headspace Technique, *J. Chrom.* **1977**, 133, 83.
14. P. A. Pella, Measurment of the Vapor Pressure of TNT, 2,4-DNT, 2,6-DNT and EGDN, *J. Anal Chem.* **1977**, 9, 301.
15. R. B. Cundall, T. F. Palmer, C. E. C. Wood, Vapor Pressure Measurements on some Organic High Explosive, *J. Trans. Faraday Chem Soc.* **1978**, 74, 1339.
16. B. C. Dionne, D. P. Roundbehrer, J. R. Achter, Hobbs, D. H. Fine, Vapor Pressure of Explosives. *J. Energ. Mater.* **1986**, 4, 447.
17. G. Edwards, R. A. W. Hill, L. E. Sutton, The Vapor Pressure of 2:4:6- Trinitrotoluene, *Trans Faraday Soc.* **1950**, 46, 423.
18. J.D. Brandner, N.M. Junk, J.W. Lawrence, J. Robins, Vapor Pressure of Ammonium Nitrate, *J. Chem. and Eng Data.* **1962**, 7, 227.

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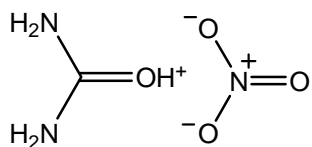
Figure 1: Structures of UN, GN, AN and TATP

Figure 2: Plot of Antoine Equation of Benzoic Acid to determine the Antoine Constants A (slope) and B (intercept).

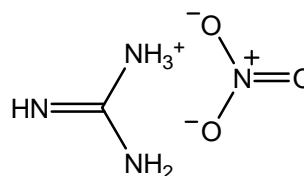
Figure 3: Thermograph of percent mass loss of urea nitrate with time (sublimation rate). The sublimation rates for urea nitrate are tabulated at the specified temperatures in Table 2

Figure 4. Thermograph of percent mass loss of guanidine nitrate with time (sublimation rate). The sublimation rates for guanidine nitrate are tabulated at the specified temperatures in Table 3.

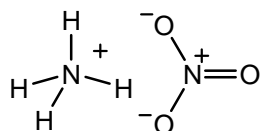
Figure 5: Clapeyron Equations for Urea Nitrate, Guanidine Nitrate, Ammonium Nitrate and Triacetone Triperoxide.



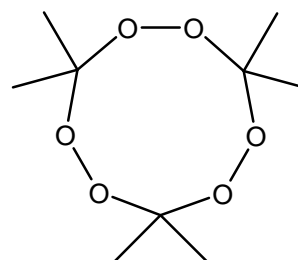
Urea Nitrate
Melting Point 133 °C(d)



Guanidine Nitrate
Melting point 213 °C(d)



Ammonium Nitrate
Melting Point 170 °C



Triacetone Triperoxide (TATP)
Melting Point 95 °C

Figure 1: Structures of UN, GN, AN and TATP

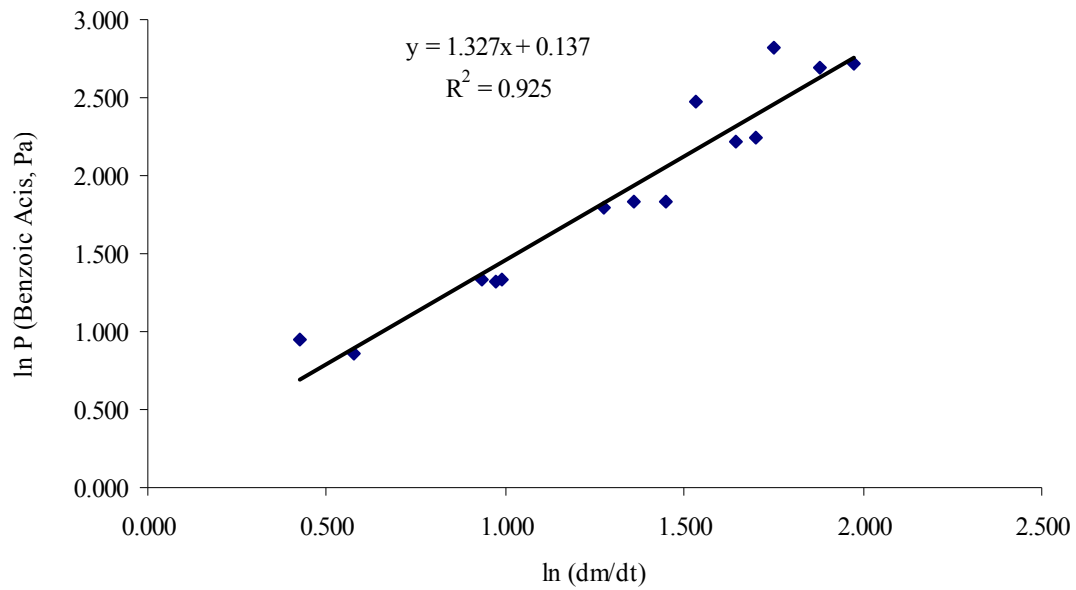


Figure 2: Plot of Antoine Equation of Benzoic Acid to determine the Antoine Constants A (slope) and B (intercept).

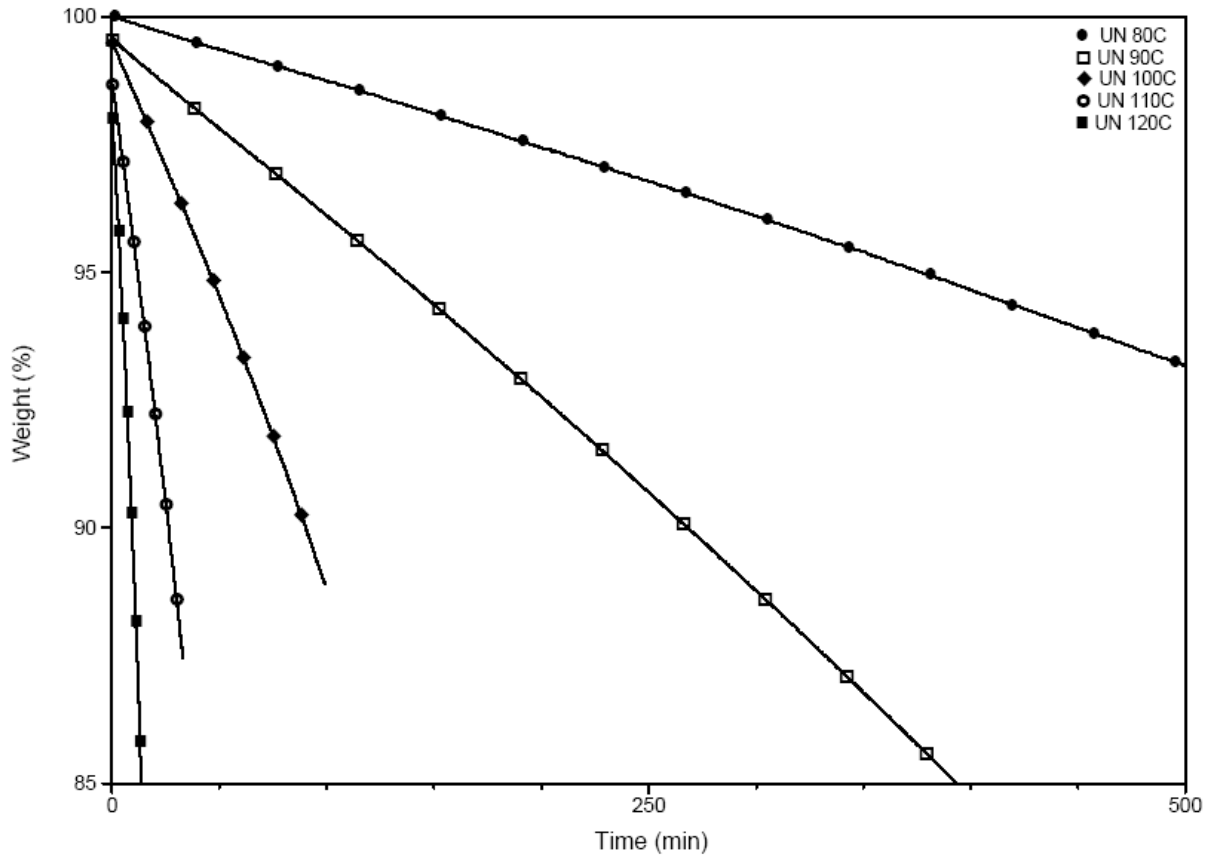


Figure 3: Thermograph of percent mass loss of urea nitrate with time (sublimation rate). The sublimation rates for urea nitrate are tabulated at the specified temperatures in Table 2.

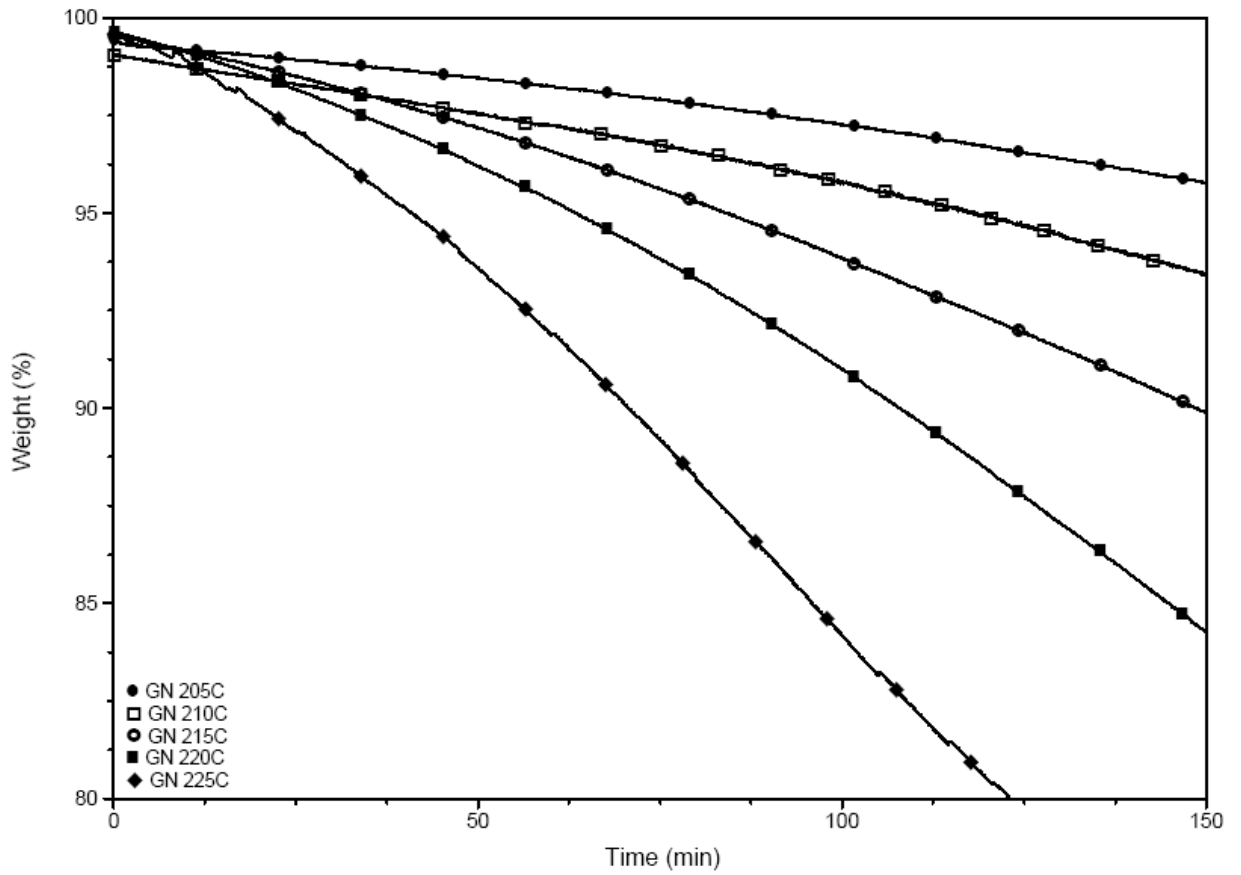


Figure 4. Thermograph of percent mass loss of guanidine nitrate with time (sublimation rate).

The sublimation rates for guanidine nitrate are tabulated at the specified temperatures in Table 3.

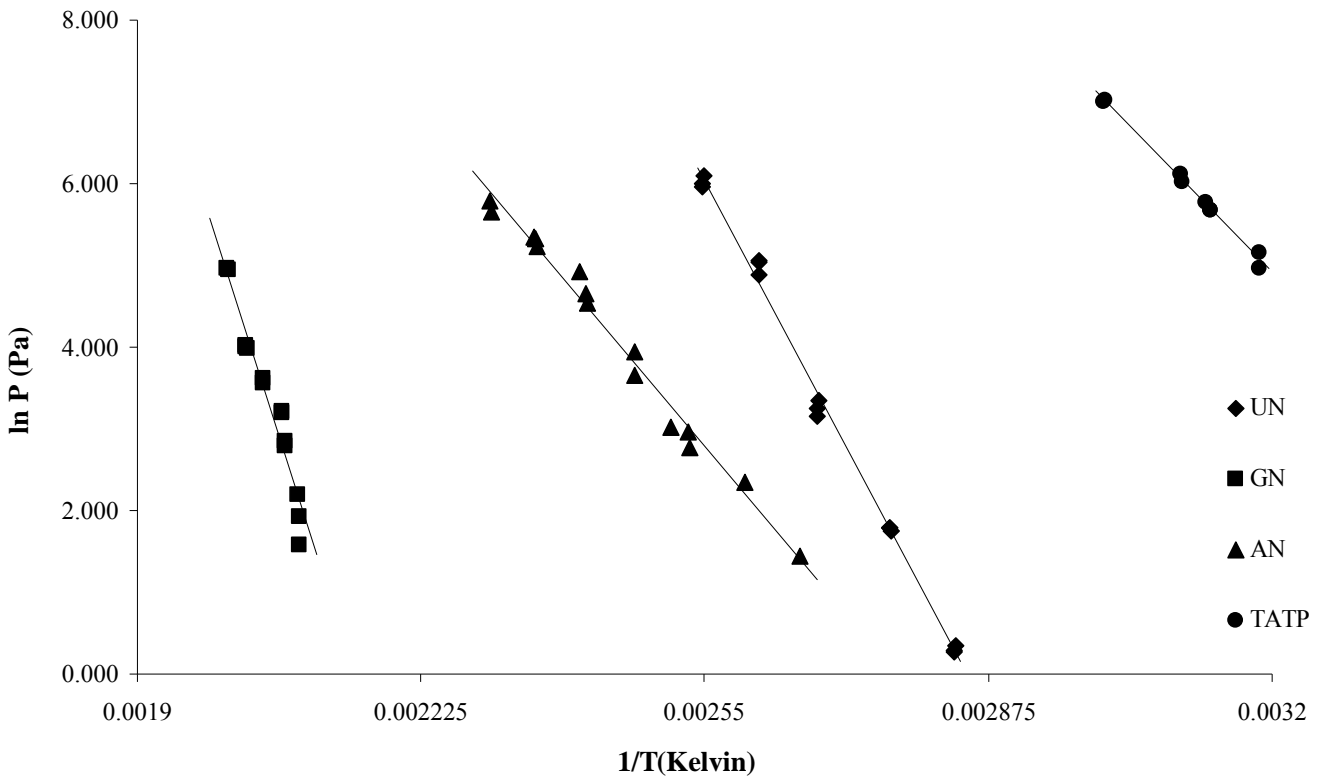


Figure 5: Clapeyron Equations for Urea Nitrate, Guanidine Nitrate, Ammonium Nitrate and Triacetone Triperoxide.

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Table 2: Sublimation rates at specified temperatures for urea nitrate (see Figure 3)

Table 3: Sublimation rates at specified temperatures for guanidine nitrate (see Figure 4)

Table 4: Sublimation rates at specified temperatures for ammonium nitrate

Table 5: Sublimation rates at specified temperatures for TATP

Table 6: Enthalpies of sublimation and vapor pressure at 25°C for UN, GN and AN

Table 1: Sublimation Rates for Benzoic Acid used in Figure 2

T (K)	std. dev	P (Pa)	dm/dt ($\mu\text{g}/\text{min}$)	ln (dm/dt)	ln P
322.084	0.172	2.376	1.779	0.576	0.865
322.881	0.698	2.588	1.527	0.423	0.951
326.367	0.161	3.731	2.649	0.974	1.317
326.527	0.077	3.793	2.548	0.935	1.333
326.531	0.070	3.795	2.692	0.990	1.334
331.064	0.121	5.989	3.587	1.277	1.790
331.458	0.065	6.225	3.899	1.361	1.829
331.475	0.163	6.235	4.258	1.449	1.830
335.519	0.174	9.197	5.181	1.645	2.219
335.787	0.264	9.432	5.470	1.699	2.244
338.255	0.202	11.862	4.620	1.530	2.473
340.629	1.279	14.715	6.564	1.882	2.689
340.913	0.232	15.095	7.197	1.974	2.714
342.153	0.264	16.856	5.755	1.750	2.825

Table 2: Sublimation rates at specified temperatures for urea nitrate (see Figure 3)

T (K)	std. dev	dm/dt ($\mu\text{g}/\text{min}$)	ln(p)	p (Pa)	p(Torr)
352.394	0.068	1.164	0.338	1.403	0.011
352.583	0.072	1.107	0.272	1.312	0.010
352.712	0.122	1.114	0.280	1.323	0.010
362.028	0.085	3.486	1.793	6.009	0.045
361.725	0.051	3.361	1.745	5.725	0.043
361.982	0.122	3.497	1.798	6.036	0.045
373.107	0.293	11.219	3.344	28.338	0.213
373.368	0.135	10.390	3.242	25.594	0.192
373.259	0.260	9.741	3.157	23.495	0.176
382.920	0.158	35.917	4.888	132.696	0.995
382.758	0.310	40.903	5.061	157.673	1.183
382.781	0.164	40.492	5.047	155.577	1.167
392.416	0.294	89.125	6.094	443.138	3.324
392.435	0.262	80.351	5.956	386.207	2.897
392.516	0.246	82.984	5.999	403.092	3.023

Table 3: Sublimation rates at specified temperatures for guanidine nitrate (see Figure 4)

T (K)	std. dev	dm/dt ($\mu\text{g}/\text{min}$)	$\ln(p)$	p (Pa)	p (Torr)
479.615	0.178	2.982	1.586	4.886	0.037
479.454	0.038	3.854	1.926	6.865	0.051
479.826	0.102	4.697	2.189	8.926	0.067
483.296	0.088	7.374	2.787	16.238	0.122
483.322	0.089	7.674	2.840	17.122	0.128
483.918	0.127	9.994	3.191	24.309	0.182
483.926	0.136	10.184	3.216	24.923	0.187
489.275	0.095	13.141	3.554	34.953	0.262
489.109	0.093	13.802	3.619	37.305	0.280
493.670	0.049	18.238	3.989	53.992	0.405
494.106	0.196	18.337	3.996	54.384	0.408
494.173	0.091	18.680	4.021	55.736	0.418
499.217	0.050	37.446	4.943	140.240	1.052
499.056	0.077	38.065	4.965	143.324	1.075

Table 4: Sublimation rates at specified temperatures for ammonium nitrate

T (K)	std. dev	dm/dt ($\mu\text{g}/\text{min}$)	$\ln(p)$	p (Pa)	p (Torr)
376.110	0.131	2.659	1.434	4.196	0.031
385.324	0.076	5.260	2.339	10.373	0.078
394.738	0.122	7.254	2.766	15.890	0.119
398.210	3.078	8.414	2.962	19.345	0.145
395.039	0.202	8.763	3.016	20.418	0.153
404.931	0.091	14.119	3.649	38.447	0.288
404.894	0.096	17.582	3.940	51.434	0.386
413.816	0.057	27.551	4.536	93.336	0.700
414.119	0.107	30.304	4.663	105.908	0.794
415.502	0.542	36.975	4.927	137.907	1.034
424.501	0.029	46.267	5.224	185.679	1.393
424.653	0.167	50.195	5.332	206.878	1.552
423.990	0.049	50.537	5.341	208.751	1.566
434.083	0.224	63.698	5.648	283.787	2.129
433.756	0.094	71.059	5.793	328.103	2.461

Table 5: Sublimation rates at specified temperatures for triacetone triperoxide

T (K)	std. dev	dm/dt ($\mu\text{g}/\text{min}$)	ln(p)	p (Pa)	p (Torr)
313.884	0.046	38.167	4.969	143.837	1.079
313.978	0.036	43.825	5.152	172.789	1.296
319.454	0.073	64.830	5.672	290.498	2.179
319.568	0.043	65.371	5.683	293.723	2.203
320.073	0.066	69.524	5.764	318.733	2.391
322.904	0.057	84.521	6.024	413.027	3.098
323.003	0.224	91.020	6.122	455.683	3.418
332.390	0.225	179.955	7.026	1125.725	8.444
332.467	0.105	176.727	7.002	1099.012	8.243

Table 6: Enthalpies of sublimation and vapor pressure at 25°C for UN, GN and AN

	ΔH_{sub} (kJ/mol)	Vapor pressure at 25°C	
		Vapor Pressure (Pa)	Vapor Pressure (Torr)
Urea Nitrate	167	3.94×10^{-5}	2.96×10^{-7}
Guanidine Nitrate	279	2.66×10^{-18}	1.99×10^{-20}
Ammonium Nitrate	106	5.98×10^{-4}	4.49×10^{-6}
TATP (this work)	91.7	24.8	0.186