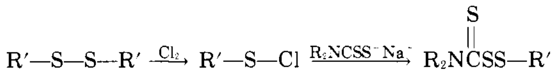
bamates with alkylsulfenyl chlorides. This method has been described by Douglass (*2*), Himel and Edwards (*4*), and Schulze *et al.* (*7*).

Alkylsulfenyl chlorides were prepared by treating carbon tetrachloride solutions of alkyl disulfides with chlorine. The following sequence of reactions illustrates this method:



$$R'{-}S{-}S{-}R' \xrightarrow[CCl_4]{Cl_2} R'{-}S{-}Cl \xrightarrow{R_2NCSS^-Na^+} R_2N\overset{\overset{S}{\|}}{C}SS{-}R'$$

When R′ was normal alkyl, the sulfenyl chloride was prepared at –20° to –25° C. in order to minimize formation of α-chloroalkylsulfenyl chlorides (*1, 3*). When R′ was *tert*-butyl, a reaction temperature of 25° to 32° C. was used. The higher temperature favors sulfur-sulfur bond cleavage in tertiary alkyl disulfides and lower temperatures favor carbon-sulfur bond cleavage (*7*).

EXPERIMENTAL

Sodium *N,N*-Di-*n*-propyldithiocarbamate. To a solution of 50.6 grams (0.5 mole) of di-*n*-propylamine in 150 ml. of water was added 39.6 grams (0.52 mole) of carbon disulfide. The reaction vessel was cooled by an ice bath, and the carbon disulfide was added at a rate sufficient to maintain a temperature of 10° to 15° C. A solution of 20.0 grams (0.5 mole) of sodium hydroxide in 50 ml. of water was then added at a rate sufficient to maintain the temperature below 15° C. The mixture was stirred for 4 hours, left at room temperature for 15 hours, and reduced to about one third the original volume by evaporation of water. This solution was cooled to obtain a solid which was collected by filtration. The solid was washed with ether and dried to obtain 55.8 grams (51.3%) of sodium *N,N*-di-*n*-propyldithiocarbamate monohydrate (m.p. 54–57° C.).

***tert*-Butylsulfenyl *N,N*-Di-*n*-propyldithiocarbamate (XII).** Chlorine(7.1 grams, 0.10 mole) was added just above the surface of a stirred solution of 17.8 grams (0.10 mole) of *tert*-butyl disulfide in 250 ml. of carbon tetrachloride. The temperature of the reaction was maintained at 20° to 30° C. by use of an ice bath. Soon after the chlorine had been added, the solution of sulfenyl chloride was added rapidly to a stirred suspension of 37.2 grams (0.17 mole) of sodium *N,N*-di-*n*-propyldithiocarbamate monohydrate in 500 ml. of carbon tetrachloride. When normal alkylsulfenyl chlorides were used, the suspension of dithiocarbamate was cooled to –25° C. before addition of the sulfenyl chloride. The cloudy solution was warmed slowly and heated under reflux for 2 hours. A suspended solid (probably sodium chloride) was removed by filtration, and the filtrate was washed with water before being dried over magnesium sulfate. Evaporation of the solvent gave a viscous liquid which was distilled through a short-path apparatus. A second distillation gave 16.3 grams (36.3%) of a yellow liquid [b.p. 128.5–35°/0.04–0.06 mm., $\lambda_{\max}^{\text{liquid film}}$ 1475 cm.$^{-1}$ (N=C=S)].

LITERATURE CITED

(1) Brower, K.R., Douglass, I.B., *J. Am. Chem. Soc.* **73**, 5787 (1951).
(2) Douglass, I.B., "Organic Sulfur Compounds," N. Kharasch, Ed., Vol. I, p. 350, Pergamon Press, New York, 1961.
(3) Douglass, I.B., Brower, K.R., Martin, F.T., *J. Am. Chem. Soc.* **74**, 5770 (1952).
(4) Himel, M., Edwards, L.D. (to Phillips Petroleum Co.), U.S. Patent **2,792,394** (May 14, 1957).
(5) Hunt, M. (to E.I. duPont de Nemours & Co.), *Ibid.*, **2,390,713** (Dec. 11, 1945).
(6) Kice, J.L., *Accounts Chem. Res.* **1**, 58 (1968).
(7) Schulze, W.A., Short, G.H., Crouch, W.W., *Ind. Eng. Chem.* **42**, 916 (1938).
(8) Watson, A.A., *J. Chem. Soc.* **1964**, 2100.

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Vapor Pressures and Heats of Sublimation of Some High Melting Organic Explosives

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A method is described for the determination of vapor pressures in the range of 10^{-5} to 10^{-9} torr. Measurements are reported on six nitro compounds: cyclotrimethylenetrinitramine, RDX; cyclotetramethylenetetranitramine, beta polymorph, β-HMX; 2,4,6-trinitroaniline, TNA; 1,3-diamino-2,4,6-trinitrobenzene, form I polymorph, DATB-I; 1,3,5-triamino-2,4,6-trinitrobenzene, TATB; and 2,2′,4,4′,6,6′-hexanitrostilbene, HNS. Relationships between heats of sublimation and intermolecular hydrogen bonding are discussed.

AS PART of a study at this laboratory directed toward the determination of the physical properties of organic high explosives, it was necessary to measure the vapor pressures of several explosives at elevated temperatures. Experiments of this type have rarely been performed before because of the poor stability of poly-nitro compounds at high temperatures, the difficulty in obtaining pure samples, etc. Recently, the need for explosives to withstand the temperature and pressure regimes imposed by space exploration has provided the impetus necessary to overcome the several experimental difficulties. This paper describes a method for the determination of vapor pressures in the range of 10^{-5} to 10^{-9} torr. Measurements are reported on six nitro compounds: cyclotrimethylenetrinitramine, RDX; cyclotetramethylenetetranitramine, beta polymorph, β-HMX; 2,4,6-trinitroaniline, TNA; 1,3-diamino-2,4,6-trinitrobenzene, form I polymorph, DATB-I; 1,3,5-triamino-2,4,6-trinitrobenzene, TATB; and 2,2′,4,4′6,6′-hexanitrostilbene, HNS.

EXPERIMENTAL

The Langmuir method was used for the determination of vapor pressures from measurements of the rates of sublimation at constant temperature (*4, 9*). Vapor pressures were computed from the observed weight loss of the sample heated in a vacuum. The expression used was:

$$P(\text{torr}) = 17.14 \times G \times (T/M)^{1/2}$$

where G is the weight loss in grams/cm^2/sec., T is the absolute temperature, and M is the molecular weight. In the calculations, a condensation coefficient of 1 is assumed. This, the authors feel, is justified by the good agreement between the results obtained from the Langmuir and Knudsen method results for RDX.

Samples were heated at a constant temperature in a glass-vacuum apparatus (Figure 1). After centering the sample holder in the jacketed section, the section was sealed and the system evacuated to at least 5×10^{-7} torr. Two types of sample holders were used (Figure 2). One consisted of a metal plate with machined, circular depressions. The other type was constructed by cutting a glass sample vial about 8 mm. from the closed end. The sample was heated by passing the vapors of a refluxing liquid through the jacket of the sample section. Two 500-ml. round-bottomed flasks heated by electric mantles and located near the ends of the jacketed region were used for the reflux liquid, and the vapors were condensed by a single water-cooled condenser located as indicated. The jacketed section was insulated with eight layers of aluminum foil.

Constant temperatures were provided by a series of liquids (Table I) maintained at the reflux point. The boiling points of the liquids were determined in the usual manner. However, the temperature at the sample is lower than the boiling point of the refluxing liquid. For example, in the case of water, this difference was 2.1° C. A temperature correction was applied for all liquids used.

Temperatures inside the vacuum apparatus at the sample position were determined for five of the liquids at reflux by sealing a chromel-alumel thermocouple inside. From the measurements of these five liquids a temperature correction curve (Figure 3) was constructed from the differences between the temperature inside the vacuum apparatus and

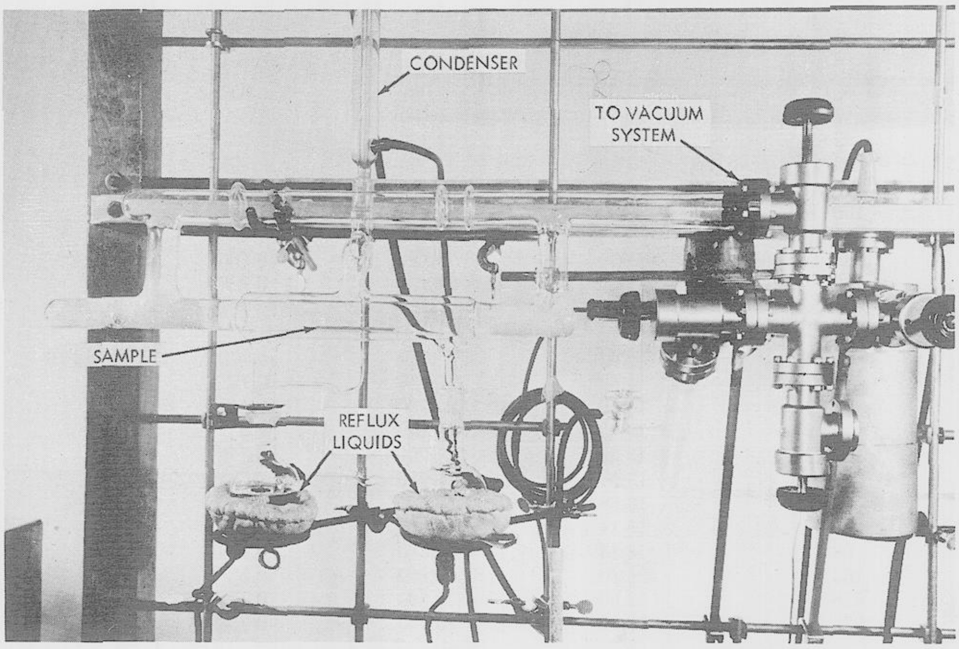

Figure 1. Vapor pressure apparatus

Table I. Temperature of Reflux Liquids

Liquid	Boiling Temp., ° C.[a]	Temp. in Vacuum Apparatus, ° C.
Methyl acetate	57.4	55.7
Methanol	64.4	62.6[b]
Benzene	80.1	78.2
n-Propanol-water azeotrope	87.3	85.3[b]
Water	99.8	97.7[b]
Toluene	110.3	108.1
n-Butanol	117.8	115.6
Chlorobenzene	131.8	129.3
m-Xylene	138.8	136.2
Anisole	152.7	150.0
Mesitylene	164.4	161.4[b]
Phenetole	169.4	166.3
o-Dichlorobenzene	180.5	177.3
Benzonitrile	189.3	185.8
Nitrobenzene	210.3	206.3[b]

[a] At 755 torr atmospheric pressure. [b] Temperatures determined by thermocouple measurements with external pressure of 755 torr.

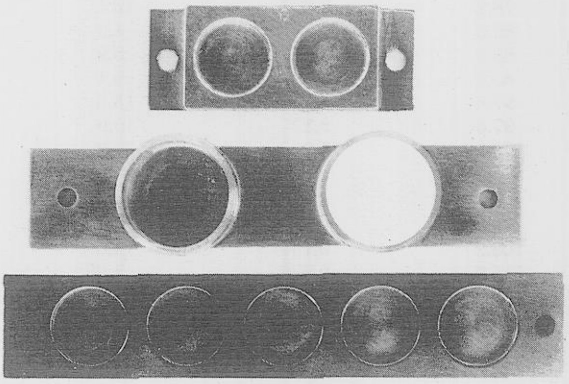

Figure 2. Sample holders

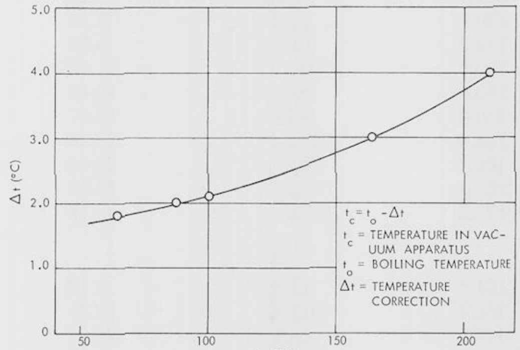

Figure 3. Temperature correction curve

the temperature of the refluxing liquid. Temperature corrections for all liquids were taken from this curve.

The uncertainty in the temperature represents the largest source of experimental error. This uncertainty is estimated to be about 0.2° to 0.3° C. in the temperatures below 150° C. for heating periods less than 72 hours. At higher temperatures and longer times, the estimated error is slightly greater, perhaps 0.5° C. Barometric pressure fluctuations affect the boiling points of the heating liquids and are likely to be a source of some error during the longer runs.

About 40 to 50 minutes are required for the sample to reach its maximum temperature after beginning to heat

Table II. Results and Data

T., ° C.	Vapor Pressure (× 10^7 Torr)	Wt. Loss (G. × 10^3)	Time, Sec.	Area, Cm.^{2}	Line Constants	
					A	*B*
			RDX			
55.7	3.50	9.63	424,080	1.355	14.18	−31,110
55.7	3.24	5.05	424,080	0.766		
55.7	3.42	5.06	424,080	0.728		
62.6	8.21	7.63	144,900	1.351		
62.6	7.14	11.54	144,900	2.35		
62.6	8.63	15.02	144,900	2.53		
78.2	69.3	45.09	177,300	0.791		
78.2	78.7	20.79	72,000	0.791		
85.3	155	53.90	57,600	1.317		
97.7	735	108.48	24,120	1.355		
97.7	667	55.72	24,120	0.766		
97.7	702	55.68	24,120	0.728		
			TNA			
55.7	5.48	4.82	235,080	0.770	12.10	−27,710
55.7	5.37	4.62	235,080	0.753		
55.7	4.80	10.60	322,200	1.410		
55.7	4.92	19.50	322,200	2.53		
62.6	10.80	13.25	331,200	0.770		
62.6	11.10	13.84	331,200	0.783		
78.2	68.0	18.86	76,680	0.770		
78.2	65.6	18.11	76,680	0.766		
78.2	68.3	18.54	76,680	0.753		
85.3	163	125.20	65,160	2.53		
97.6	628	52.60	23,760	0.770		
97.6	625	53.19	23,760	0.783		
			DATB-I			
62.6	0.081	3.3	303,200	6.33	13.73	−33,470
78.2	0.879	12.4	459,360	6.33		
85.3	2.36	4.9	68,400	6.33		
85.3	2.25	5.9	86,400	6.33		
85.3	2.09	5.1	80,280	6.33		
97.6	9.80	15.3	52,200	6.33		
97.6	9.12	15.9	58,320	6.33		
108.1	34.0	31.0	30,960	6.33		
			β-HMX			
97.6	0.0324	3.7	3,456,000	6.33	16.18	−41,890
108.2	0.164	4.6	860,400	6.33		
115.6	0.390	1.97	424,080	2.34		
115.6	0.385	1.98	424,080	2.38		
115.6	0.419	2.09	424,080	2.31		
129.3	2.83	4.92	145,800	2.38		
129.3	2.87	4.83	145,800	2.31		
			TATB			
129.3	0.733	4.06	845,280	1.403	14.73	−40,210
129.3	0.746	4.10	845,280	1.392		
136.2	1.83	6.36	315,000	2.38		
136.2	1.93	6.50	315,000	2.31		
150.0	10.3	11.02	172,800	1.355		
150.0	9.42	10.41	172,800	1.403		
150.0	9.73	10.67	172,800	1.392		
161.4	32.2	29.28	86,400	2.34		
161.4	32.3	29.00	86,400	2.31		
166.4	45.8	42.09	86,400	2.38		
177.3	167.0	49.16	28,440	2.34		
			HNS			
161.4	0.396	4.10	688,680	2.53	14.19	−43,010
166.4	0.592	12.8	578,880	6.33		
177.3	2.15	22.9	288,000	6.33		
185.8	4.97	12.25	168,480	2.53		
206.3	39.4	36.55	64,800	2.53		

the reflux liquid. This time interval was determined by following the temperature increase at the sample position as a function of time. To determine time intervals for the experimental runs, a time of 40 minutes after the initiation of heating was used as time zero. At the completion of the heating period, the jacketed section was cooled with an air gun for about 15 minutes, after first removing a part of the aluminum foil insulation. The error in the measurement of the heating interval is probably about 0.2 hour.

The vacuum system consists of an 8-liter-per-second Varian Vac Ion pump and a Varian titanium sublimation pump connected to a stainless steel manifold. The manifold is a cross fitting with four stainless steel, high vacuum valves in the arms of the cross. One valve isolates the pumps from the system, a second valve isolates a forepump. The remaining two valves connect two glass-jacketed units to the vacuum system through glass-to-metal seals. All glass parts are made of 1.5-inch i.d. borosilicate glass tubing. Each unit may be operated independently.

All of the samples were carefully purified by repeated recrystallization and thoroughly dried to remove residual solvent. In general, these materials represent the highest quality available for study. The purity of the samples was tested by at least one of the following techniques in each case: thin layer chromatography, melting point, or gas chromatography. The compounds in this work have all been studied at temperatures far higher than any used in the determination of vapor pressures. At these elevated temperatures no decomposition was detected, as determined by gas evolution techniques (*11*) and thin layer chromatography (*7*).

HMX has four well-characterized polymorphs. β-HMX is stable up to 102° C., although it does not undergo a solid-solid transition until well above 150° C. Thus, all of the measurements on β-HMX except the one at 97.6° C. are in the temperature range where this crystal modification of HMX is unstable. It was necessary to heat β-HMX for 40 days at 97.6° C. to obtain a measurable loss in weight. At the completion of this run, the apparatus was rinsed with acetone. All of the sublimed material was collected and identified as β-HMX by refractive index measurements, indicating no decomposition had occurred. Upon completion of the run at the highest temperature, 129.3° C., the sample was examined by x-ray diffraction, and the β-polymorph was still present.

DATB has two well-characterized polymorphs, the I→II transition occurring at 217° C. In contrast to HMX, DATB easily undergoes this transition even in the solid phase, which may be explained by the higher vapor pressure of DATB. However, the highest temperature used for DATB-I in these vapor pressure measurements (108° C.) is over 100° lower than the transition point. At these relatively low temperatures, no detectable amount of I→II conversion has ever been found.

RESULTS AND DISCUSSION

The vapor pressures of the compounds at the temperatures of the experiments are reported in Table II along with a summary of the experimental data. The least squares fits of the vapor pressures to the equation:

$$\log_{10} P = B/(4.576 \times T\,°\text{K.}) + A$$

are given in Figures 4 through 9. The line constants *A* and *B*, *B* representing the heat of sublimation, are also given in Table II.

The vapor pressure of RDX is in good agreement with the data obtained by the National Bureau of Standards (NBS) using a Knudsen cell (*10*). The NBS sample, supplied by this laboratory, was a part of the same sample used in this work. Vapor pressure measurements on RDX by Edwards using a Knudsen cell are somewhat higher, although his data at 131° and 138° C. would appear to be in reasonable agreement with the other data (*5*).

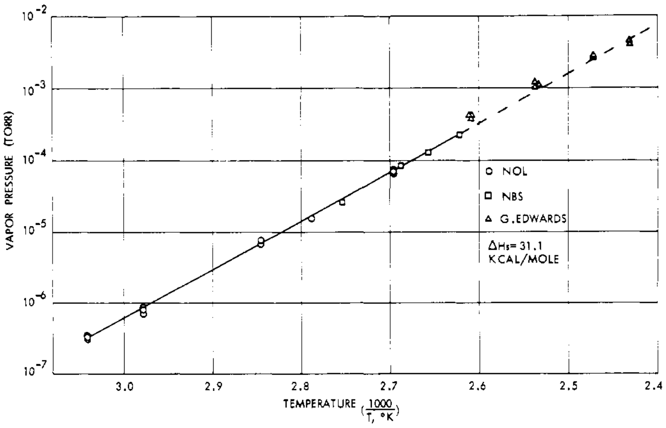

Figure 4. Vapor pressure of RDX

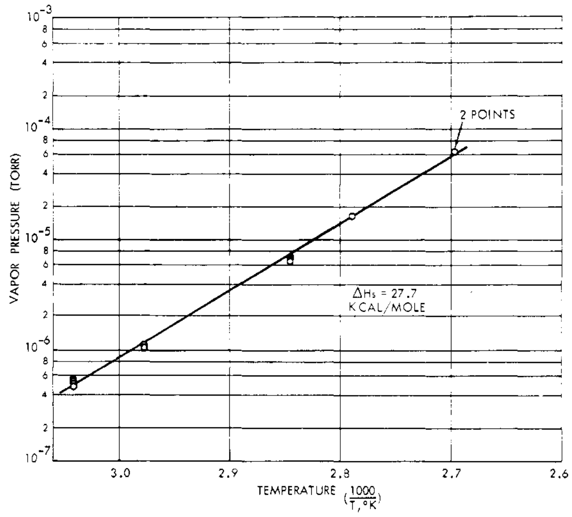

Figure 5. Vapor pressure of TNA

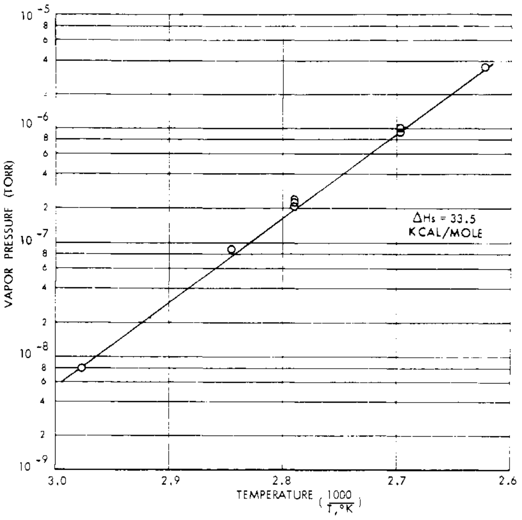

Figure 6. Vapor pressure of DATB-I

Ignoring any effects caused by not correcting to a standard temperature, several interesting observations may be made on the heats of sublimation and the properties of the compounds. The difference between the molar heats of sublimation of RDX and β-HMX, 10.78 kcal. per mole, apparently is largely a function of molecular weight. This is indicated by the specific heats of sublimation, 140.0 and 141.4 cal. per gram, respectively, and agrees with the known structures of β-HMX (*2*) and RDX (*6*) which indicate no marked difference in intermolecular forces.

The trend in the molar heats of sublimation in the series

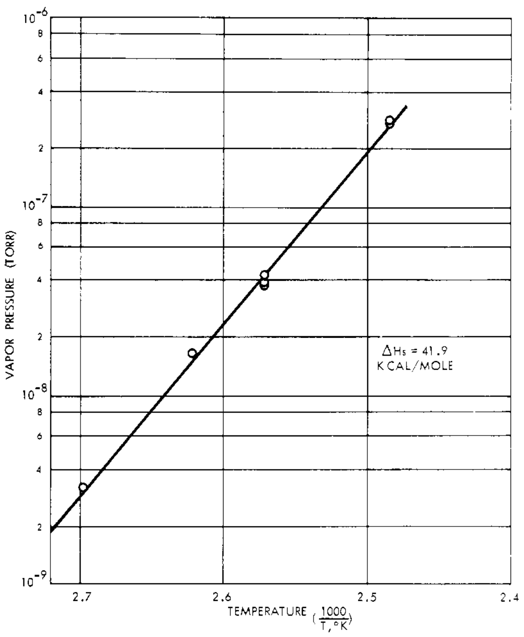

Figure 7. Vapor pressure of β-HMX

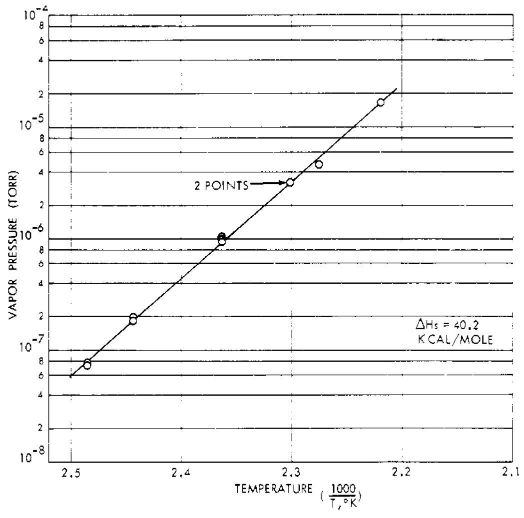

Figure 8. Vapor pressure of TATB

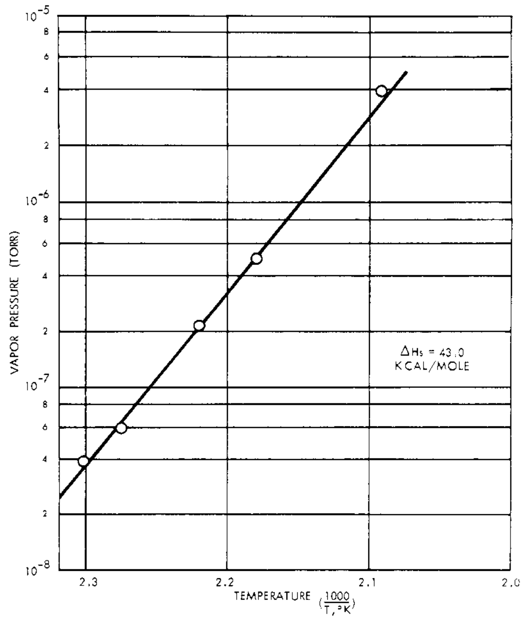

Figure 9. Vapor pressure of HNS

Table III. Heats of Sublimation

Compound	Molar Heat of Sublimation, Kcal.[a]	Specific Heat of Sublimation, Cal./G.	Mol. Wt.	Mid-point of Temp. Range, ° C.
RDX	31.11	140.0	222.2	76.70
β-HMX	41.89	141.4	296.2	113.45
TNA	27.71	121.5	228.1	76.65
DATB-I	33.47	137.6	243.2	85.35
TATB	40.21	155.7	258.2	153.30
HNS	43.01	95.5	450.3	183.85

[a] For intercomparison these should be corrected to the same temperature. Unfortunately, no data exist concerning the heat capacities of these compounds as solids and gases, and the authors feel no correction is better than a poorly founded one.

of trinitro-aromatic amines persists, even when the specific heats are considered (Table III). This trend agrees, at least in a qualitative sense, with what is known about the structures of these solids, based on published crystal structure determinations. The structures of DATB-I (*8*) and TATB (*1*) are quite different. The former is hydrogen bonded into chains with two intermolecular hydrogen bonds per molecule within the chains and only weak interactions between the chains. TATB, however, is hydrogen bonded into a layered structure with six strong intermolecular hydrogen bonds per molecule. Although the structure of TNA has not been reported, the structures of similar compounds such as *p*-nitroaniline (*12*) and 2,3,4,6-tetranitroaniline (*3*) have been determined. These compounds exhibit hydrogen bonding schemes similar to one another and weaker than that found either in DATB-I or TATB, based on the intermolecular separation between amino and nitro functional groups. If the structure of TNA is comparable to these compounds, at least with respect to intermolecular hydrogen bonding, then the intermolecular forces due to this cause in TNA should be smaller than in DATB-I, which in turn should have smaller forces than TATB. Thus, ignoring other factors which affect the heats of sublimation (polarity, dispersion, temperature, etc.), the trends in intermolecular hydrogen bonding and heats of sublimation, within this series of polynitro-aromatic amines, parallel one another in a qualitative sense. A more exact discussion would require inclusion of the factors ignored here, as well as some method for estimating the strengths of hydrogen bonding systems that is more meaningful than internuclear separation.

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Cady, H.H., Larson, A.C., *Acta Cryst.* **18**, 485 (1965).
(2) Cady, H.H., Larson, A.C., Cromer, D.T., *Ibid.*, **16**, 617 (1963).
(3) Dickinson, Charles, Stewart, J.M., Holden, J.R., *Ibid.*, **21**, 663 (1966).
(4) Dushman, S., Lafferty, J.M., "Scientific Foundations of Vacuum Technique," 2nd. ed., Wiley, New York, 1962.
(5) Edwards, G., *Trans. Faraday Soc.* **49**, 152 (1953).
(6) Harris, P.M., DDC, Cameron Station, Alexandria, Va., **AFOSR TR-59-165**, 1959.
(7) Hoffsommer, J.C., U. S. Naval Ordnance Lab, Silver Spring, Md., private communication, 1967.
(8) Holden, J.R., *Acta Cryst.* **22**, 545 (1967).
(9) Langmuir, I., *Phys. Rev.* **2**, 329 (1913).
(10) Miller, R.G., Prosen, E.J., Natl. Bur. of Standards, Washington, D. C., private communication, 1953.
(11) Rosen, A.H., Simmons, H.T., DDC, Cameron Station, Alexandria, Va., **NAVORD 6629**, 1959.
(12) Trueblood, K.N., Goldish, E., Donohue, J., *Acta Cryst.* **14**, 1009 (1961).

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