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THERMAL DECOMPOSITION OF ENERGETIC MATERIALS. 23. THERMOCHEMICAL DIFFERENTIATION OF CYCLIC AND ACYCLIC NITRAMINES BY THEIR PHASE TRANSITIONS

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ABSTRACT

The sum of the values of ΔH measured by differential thermal analysis for the phase transitions from room temperature through the melting point for seven cyclic nitramines and nitrosamines is 35 ± 4 cal g^{-1}. ΔS_f for these compounds is 0.06 ± 0.03 cal deg^{-1} g^{-1}. The values for $\Sigma\Delta H$ and ΔS_f for ten acyclic nitramines are 66 ± 18 cal g^{-1} and 0.17 ± 0.07 cal deg^{-1} g^{-1}, respectively. The statistically significant difference between these two classes probably originates from the shape of the molecules. The disordered high-temperature phase of 1,4-dinitrofurazano[3,4-*b*]piperazine (DNFP), previously discovered by IR spectroscopy, is confirmed by DTA to be a plastic phase.

INTRODUCTION

Studies of the fast thermal decomposition of energetic materials point to several connections between the parent molecular structure and the first observed decomposition products [1–3]. For many of the compounds a search was also conducted to locate the solid–solid phase transitions [4–11]. This is because solid phase properties of high energy compounds can sometimes present practical difficulties in their preparation and use. A classic example is the well-known chemical propellant and explosive, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) which possesses three known polymorphs [12–14] and a hydrate [15]. The density and crystal morphology of these polymorphs differ. Should a solid–solid phase transition take place from one phase to another when HMX is a component of a formulation, then strains and voids may develop with potentially disastrous consequences. Moreover, α-HMX, which is easily obtained under certain crystallizing conditions, is more shock sensitive than β-HMX [13].

In the course of the present research, numerous new solid phases of many energetic materials were discovered by the use of a combination of DTA and IR spectroscopy. Several rather unexpected observations were made. The previously known [16] plastic phase of TRDX was determined by solid state

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NMR spectroscopy [17] to be better described as a "crystal liquid" wherein the crystal shape is retained but the molecules display considerable translational motion. Both DATH [8] and BCEN [10] were found to have amorphous solid phases that slowly crystallize. Complex polymorphic schemes were mapped for 1,3,5,7-tetranitro-3,7-diazabicyclo[3.3.1]nonane (TNDBN) [6], DNFP[7], OHMX[11], and 3,7-dinitro-1,3,5,7-tetrazabicyclo[3.3.1]nonane (DPT) [6]. Despite the chance for limited success, it was hoped that these studies would improve, even slightly, the understanding of some of the factors that contribute to the presence or absence of extensive polymorphism in related molecules. Unfortunately, this relationship continues to be elusive, undoubtedly because the details of the crystal structure and vibrational amplitudes need also to be considered. Detailed studies on closely related compounds appear to be needed to gain this level of understanding [18]. However, it was discovered that the thermal parameters associated with the solid–solid phase transitions and melting are distinctly different for cyclic and acyclic nitramines.

EXPERIMENTAL

Samples of the compounds were supplied by Drs. R.L. Willer (Morton-Thiokol), D. Levins (CSD, United Technologies), H. Adolph (NSWC), D.O. Woolery (Rocketdyne), and G.W. Nauflett (NSWC). Thermograms were recorded on a Mettler 2000B DTA which was calibrated by the use of indium metal. Five mg of sample and a heating rate of 5 K min^{-1} in N_2 were used. The endotherms were measured from the beginning to the end of the pen deflection associated with a given process. The error in the values of ΔH and ΔS is estimated to be ± 5%.

RESULTS AND DISCUSSION

Several of the compounds described here display complex solid–solid phase transition schemes. ΔH for the temperature-induced solid–solid phase transitions up to the melting point was summed and designated as ΔH_t. Five polymorphs of OHMX [11] and TNDBN [6] were discovered above 293 K. Four polymorphs of DNFP [7] were eventually detected above 293 K. DATH [8] and BCEN [10] have a crystalline and an amorphous state, while DPT [6] exhibits two crystalline phases. The solid phase preceding melting of DPT and TNDBN appears to be highly disordered based on the linewidths in the IR spectrum [6,7] and is probably a plastic phase. Unfortunately, decomposition accompanies the melting of these two compounds which precludes the measurement of true values of ΔH_f and ΔS_f, the enthalpy and entropy of fusion. These two compounds and several others,

TABLE 1

Enthalpies of the solid–solid phase transitions and fusion, and the entropy of fusion for cyclic nitramines

Acronym	Formula	MP (K)	ΔH_t [a] (cal g^{-1})	ΔH_f (cal g^{-1})	ΔH_{t+f} (cal g^{-1})	ΔS_f (cal deg^{-1} g^{-1})
DNCP[3]	$CH_2N(NO_2)CH_2N(NO_2)CH_2$	410	–	37	37	0.09
DNNC[4,19]	$CH_2N(NO_2)CH_2C(NO_2)_2CH_2N(NO_2)$	430	–	30	30	0.07
DNFP[7]	$CH_2N(NO_2)CNONCN(NO_2)CH_2$	403	41	2	43	0.005
DNTO[1]	$(HCNHC(CF_3)_2N(NO_2)CH)_2$	440	2	35	37	0.08
MRDX[20]	$N(NO_2)CH_2N(NO)CH_2N(NO_2)CH_2$	446	–	32	32	0.07
RDX[21]	$N(NO_2)CH_2N(NO_2)CH_2N(NO_2)CH_2$	465	–	36	36	0.08
TRDX[17,20]	$N(NO)CH_2N(NO)CH_2N(NO)CH_2$	380	24	8	32	0.02
Average					35 ± 4	0.06 ± 0.03

[a] $\Sigma \Delta H$ for solid–solid phase transitions above 293 K.

TABLE 2

Enthalpies of the solid–solid phase transitions and fusion, and the entropy of fusion for acyclic nitramines

Acronym	Formula	MP (K)	ΔH_t[a] (cal g^{-1})	ΔH_f (cal g^{-1})	ΔH_{t+f} (cal g^{-1})	ΔS_f (cal deg^{-1} g^{-1})
BCEN[10]	$NCCH_2CH_2N(NO_2)CH_2CH_2CN$	327	–	64	64	0.20
BCMN[10]	$NCCH_2N(NO_2)CH_2CN$	367	–	66	66	0.18
DATH[8]	$N_3CH_2N(NO_2)CH_2N(NO_2)CH_2N(NO_2)CH_2N_3$	406	–	30	30	0.08
DMEDNA[22]	$CH_3N(NO_2)(CH_2)_2N(NO_2)CH_3$	410	–	81	81	0.20
DMHDNA[22]	$CH_3N(NO_2)(CH_2)_6N(NO_2)CH_3$	331	–	63	63	0.19
DMNA[22]	$CH_3N(NO_2)CH_3$	327	–	100	100	0.30
EDNA[22]	$HN(NO_2)CH_2CH_2N(NO_2)H$	450	–	47	47	0.11
MBNA[22]	$CH_3N(NO_2)(CH_2)_3CH_3$	331	–	68	68	0.21
MEDINA[22]	$HN(NO_2)CH_2N(NO_2)H$	371	–	63	63	0.17
OHMX[11]	$CH_3(N(NO_2)CH_2)_3N(NO_2)CH_3$	490	14	61	75	0.05
Average					66 ± 18	0.17 ± 0.07

[a] $\Sigma \Delta H$ for solid–solid phase transitions above 293 K.

including HMX, would have been useful to have for Table 1, but are not included because the thermochemistry of melting and decomposition is not clearly separated.

Table 1 lists cyclic nitramines and nitrosamines for which ΔH_t, ΔH_f and ΔS_f could be cleanly measured. Table 2 lists these values for acyclic nitramines measured under the same conditions as the cyclic nitramines.

The sum of ΔH_f and ΔH_t corresponds to the enthalpy change associated with heating the molecule in the crystal lattice from room temperature to its translationally mobile molten state. One can imagine that molecules whose exterior shape and electrostatics are similar might have comparable values of ΔH_{t+f}. Consistent with this notion, $\overline{\Delta H}_{t+f}$ for the cyclic nitramines and nitrosamines in Table 1 is 35 ± 4 cal g^{-1}, whereas for the chain-like acyclic nitramines in Table 2, $\overline{\Delta H}_{t+f}$ is nearly twice as great (66 ± 18 cal g^{-1}). These data indicate that more energy on average is required to mobilize linear nitramine molecules than cyclic nitramines from room temperature to their molten state. Thus, the general molecular shape of nitramines influences the magnitude of ΔH_{t+f}. The individual values of ΔH_{t+f} and ΔH_f do not correlate with any simple variable of these molecules, such as the O to H ratio (a crude measure of the number of $C-H \cdots O$ interactions), the number of NO_2 groups (a possible measure of the $O \cdots N$ interactions), the melting point or the density.

The entropy of fusion, ΔS_f, is also distinctive in relation to the molecular shape for the cyclic nitramines in Table 1, $\overline{\Delta S}_f = 0.06 \pm 0.03$ cal deg^{-1} g^{-1} (0.08 ± 0.02 cal deg^{-1} g^{-1} excluding the plastic crystals, TRDX and DNFP). For the acyclic nitramines in Table 2, $\overline{\Delta S}_f = 0.17 \pm 0.07$ cal deg^{-1} g^{-1}. The cyclic nitramines are more internally constrained than the quasi-cylindrical acyclic molecules. Since more rigid molecules have fewer degrees of freedom, $\overline{\Delta S}_f$ should be less on average, as is observed.

Approximate values of ΔH_{t+f} and ΔS_f can be estimated on the basis of a molecular feature, namely whether the compound is a cyclic or an acyclic nitramine. Confidence in an individual number is less warranted than a range of numbers because the details of the crystal structure have not been included. Going a step further, the thermochemistry of the phase transitions fails to indicate the tendency to exhibit polymorphism.

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