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SUBLIMATION OF AMMONIUM AZIDE BY DIFFERENTIAL SCANNING CALORIMETRIC AND THERMOGRAVIMETRIC ANALYSES

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ABSTRACT

The kinetics of sublimation of ammonium azide have been investigated over the temperature range 360–389 K in a continuous flow of dry argon by thermogravimetry (TG). Sublimation follows zero-order kinetics with a corresponding activation energy of 93.3 kJ mol^{-1} which is slightly higher than its heat of sublimation (73.4 kJ mol^{-1}) determined from differential scanning calorimetric (DSC) cooling thermograms. The mechanism for sublimation is critically discussed with reference to ammonium perchlorate and ammonium halide systems. It is suggested that ammonium azide undergoes molecular sublimation and that the vapor readily dissociates above 418 K into NH_3 and HN_3. The heat of formation of 185.6 kJ mol^{-1} was deduced for gaseous NH_4N_3.

INTRODUCTION

Ammonium azide (NH_4N_3) is generally classified as an inorganic azide yet it is the only one which exhibits extensive hydrogen bonding [1,2] in the solid state. This chemical bonding gives it unique properties compared with the other inorganic azides, which are either ionic or covalent in character. When decomposed it yields ammonia, hydrogen and nitrogen [3] according to eqn. (1).

$$NH_4N_3(s) \rightarrow NH_3(g) + \tfrac{1}{2}H_2(g) + \tfrac{3}{2}N_2(g) \qquad (1)$$

Despite its relatively small exothermicity [4] (-158.8 kJ mol^{-1}) it is capable of considerable brisance [5] owing to the rapid evolution of gaseous products. Thus, besides being used as a weak explosive, its potential application as a gas generator has received increasing attention in recent years. It has been suggested [6] that a mixture of ammonium azide with a suitable

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oxidizer could, when properly ignited, be used to inflate safety cushions in automobiles. Others [7] have described its application as a solid propellant in photochemical micro-rockets used for altitude control.

The high volatility and thermal instability of ammonium azide had been noted by Gray and Waddington [3] who reported that in a heated vessel containing an inert gas atmosphere, the salt underwent only sublimation below 523 K. Slow decomposition sets in at higher temperatures and above the temperature limit for slow decomposition, the salt exploded. Curtius and Rissom [8] reported that the salt readily sublimed when left uncovered. The vapor was unstable and completely dissociated at 373 K. Frost et al. [9] measured its vapor pressure over the temperature range 298–403 K and found the Clausius–Clapeyron equation (2) was obeyed.

$$\log P = 11.325 - \frac{3428.6}{T} \tag{2}$$

From this equation, the latent heat of sublimation, ΔH_{sub}, of 65.8 kJ mol^{-1} can be calculated. On the other hand, Luft [10] measured its sublimation pressure and reported a much higher value of 163.4 kJ mol^{-1} for ΔH_{sub}. This inconsistency in the value of ΔH_{sub} has prompted us to undertake a direct measurement using differential scanning calorimetry (DSC) and a study of its sublimation kinetics by weight-loss measurements using thermogravimetry (TG).

EXPERIMENTAL

Analar grade sodium azide NaN_3 (BDH) was used to prepare NH_4N_3 according to the method of Frierson [11]. The ammonia gas used was of ultra-high purity grade. The sample thus prepared was stored in a desiccator over silica gel before use. A Stanton Redcroft TG 750 thermobalance and a Mettler DSC-30 were used for thermal analysis. In the TG study, a 1-mg sample was placed in an aluminum weighing pan. The pan was subsequently sealed with a cover-lid using a hand press and a pin hole made in the lid to provide free passage for the evolved gases. The furnace was held constant for 30 min at a preset value to ±0.5 K before the pan was finally inserted and placed in position. Isothermal and dynamic runs were carried out in a current of dry argon at a flow rate of 1.7×10^{-4} l s^{-1}. In the dynamic DSC study, a sample of 0.2 mg was placed inside a sealed aluminum pan of capacity 40 mm^3. Indium was used as a standard for calibration. Scan speeds chosen were 10 and 20 K min^{-1} over the temperature range 303–513 K. A Mettler TC 10 processor was used for temperature programming and to evaluate such parameters as peak temperature and enthalpy change.

RESULTS AND DISCUSSION

Enthalpy of sublimation

Upon heating at a rate of 10 K min^{-1}, the DSC thermogram of NH_4N_3 displayed a broad endotherm with an onset temperature of 333 K and a peak temperature, T_m, of 378 K (Fig. 1, curve a). There was no other peak in the thermogram even up to 700 K. This broad endotherm is characteristic of sublimation. A dynamic TG curve taken at the same heating rate shows that weight loss commences at 318 K and that the solid completely sublimes at 408 K (Fig. 2). When the heating rate was increased to 20 K min^{-1}, the same DSC trace was obtained except that the area under the curve was slightly increased; from 91.5 to 94.6 kJ mol^{-1} (Table 1). It is a composite peak with a small yet clearly discernible peak immediately after the first major peak (Fig. 1, curve a). This composite nature of the endotherm implies the two separate processes are taking place during the DSC scan. If the vapor is not allowed to escape by having the pan sealed using a hand press, the dynamic DSC trace then reveals a bodily up-shift of the endotherm (Fig. 1, curve b) from $T_m = 378$ K to $T_m = 418$ K. Its composite nature is best revealed when a cooling thermogram is subsequently taken from 473 to 303 K at a rate of

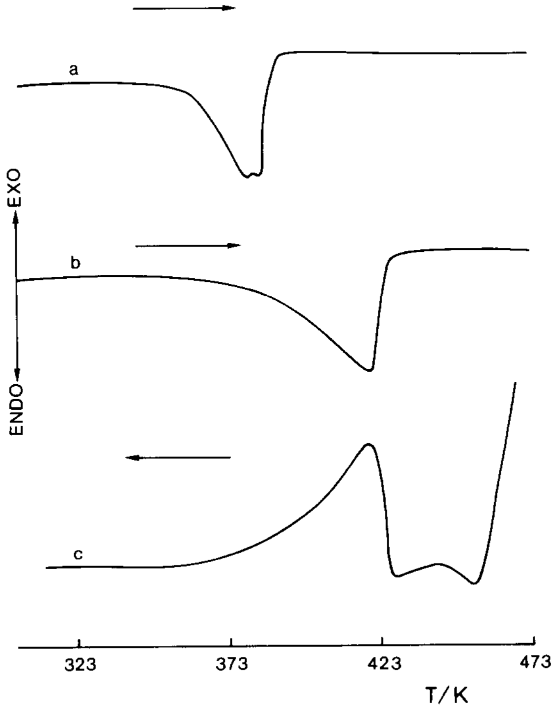
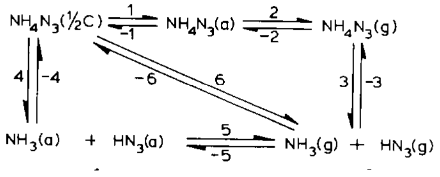


Fig. 1. DSC thermograms of NH_4N_3. (a) Open pan; (b) sealed pan; (c) taken after curve (b). The arrows indicate heating (→) and colling (←). Vertical axes not to scale.

20 K min^{-1} (Fig. 1, curve c). There is a small exotherm with $T_m = 439$ K which is immediately followed by a very much larger one with $T_m = 418$ K. The areas under the curve are in the ratio of 1 : 17. In order to identify the processes that are related to these two peaks, we first consider the various possible routes by which NH_4N_3 could undergo sublimation



(3)

Here, ½C refers to the half crystal site (such as a kink on the surface) where the molecule is only half-coordinated and is thus energetically a favorable reaction site. The molecule NH_4N_3 once formed, or its dissociated species

TABLE 1

Enthalpy change, ΔH, and peak temperature, T_m, from DSC thermograms

Sample pan	Rate (K min^{-1})	Heating		Cooling	
		ΔH (kJ mol^{-1})	T_m (K)	ΔH (kJ mol^{-1})	T_m (K)
With	10	91.5	378	–	–
hole	20	94.6	378	–	–
Sealed	10	98.8	418	–	–
	20	105.1	419	73.6	418
				4.3	419

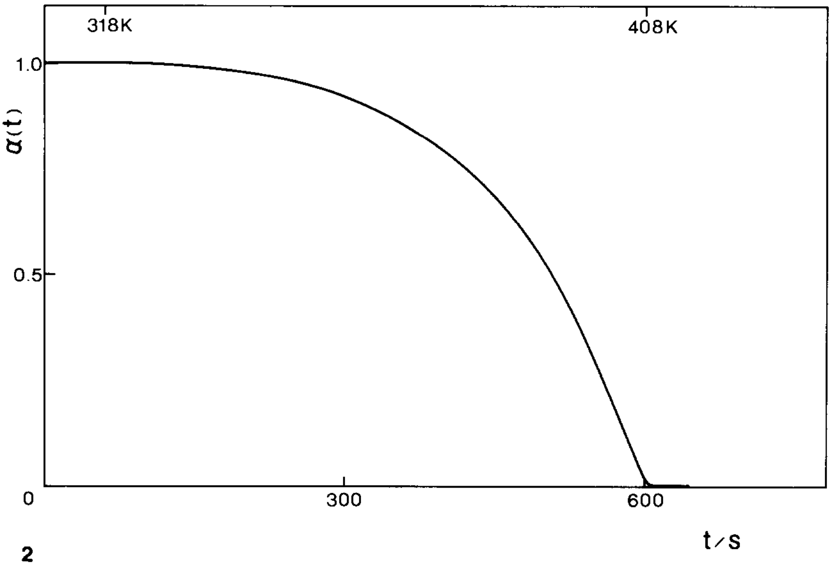


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Fig. 2. A dynamic TG trace. Heating rate, 2 K min^{-1}.

NH_3 and HN_3, will diffuse away from the kink site and become physically absorbed at the sites of less bonding energy (such as a ledge site) before it desorbs into the gas phase (g). Because of the composite nature of the sublimation endotherm and the well-resolved condensation exotherms, sublimation of NH_4N_3 via a single step (labelled 6) can be ruled out. Thus, there remain only two possible routes which are considered below.

Sublimation of other ammonium salts such as the perchlorate NH_4ClO_4 [12] and the halides NH_4X [13] follows a dissociation mechanism (analogous to steps 4 and 5 in eqn. 3) in which a proton is transferred from an NH_4^+ ion to an adjacent X^- anion thus forming the adsorbed species NH_3(a) and HX(a) whose desorption into the vapor phase (step 5) is the rate-determining step. Unlike the perchlorate and the halides (with the exception of the fluoride) there is no free NH_4^+ ion in the crystal lattice of NH_4N_3. The $H_4N{-}N_3$ bond distance is much shorter owing to the formation of four H-bonds arranged tetrahedrally about each NH_4 entity [1,2]. It is clearly of interest to find out if ammonium azide also sublimes via a dissociation mechanism like these other ammonium salts.

From the vapor pressure measurement, two values for ΔH_{sub} had been reported. However, the higher value obtained by Luft [10] (163.4 kJ mol^{-1}) falls close to that which can be calculated from published heat of formation, ΔH_f, values. For example, using data from [4,14] we calculate a value of 141.4 kJ mol^{-1} for the reaction

$$NH_4N_3(s) \rightarrow NH_3(g) + HN_3(g) \qquad (4)$$

On the other hand, the value of 65.8 kJ mol^{-1} deduced by us from the data of Frost et al. [9] (see eqn. 2) is far too low and the discrepancy cannot be accounted for by their experimental error. It is in fact likely that they were measuring the vapor pressure of gaseous NH_4N_3 vapor. We suggest that their value is for the reaction

$$NH_4N_3(s) \rightarrow NH_4N_3(g) \qquad (5)$$

It appears that in the cooling thermogram (Fig. 1, curve c) the high-temperature peak at $T_m = 439$ K refers to the recombination of HN_3 and NH_3. Since this recombination takes place entirely in the vapor phase, the area under the curve should not be taken quantitatively. The peak at 418 K is the condensation of NH_4N_3 vapor, which is the reverse of sublimation. That the low-temperature peak is condensation and the high-temperature peak is recombination is further substantiated by repetitive heating and cooling of the same sample. Upon heating, both endotherms overlap but upon cooling the two exotherms are well resolved. This heat of sublimation of 73.6 kJ mol^{-1} compares favorably with the value of 65.8 kJ mol^{-1} which we calculated from the data of Frost et al. [9]. It is more reliable since the value was obtained from a direct measurement on the heat changes by DSC. With this value, and the Gray and Waddington [3] value of 112.0 kJ mol^{-1} for

ΔH_f of $NH_4N_3(s)$, we deduce ΔH_f for $NH_4N_3(g)$ to be 185.6 kJ mol^{-1} from eqn. (5).

Considering now the equation

$$NH_4N_3(g) \rightarrow HN_3(g) + NH_3(g) \qquad (6)$$

we can insert the published ΔH_f values for $HN_3(g)$ and $NH_3(g)$, which are 299.5 and −46.2 kJ mol^{-1}, respectively, to obtain a value for the heat of reaction of 67.7 kJ mol^{-1}. It should be noted that the values of ΔH for sublimation (eqn. 5) and for dissociation (eqn. 6) are very close. This reflects the ease of dissociation of the NH_4N_3 vapor. The peak temperature, T_m, of 418 K (Fig. 1) probably marks the temperature limit at which the vapor is stable. This supports the conclusion that the measurement of the vapor pressure in the temperature range 298–403 K by Frost et al. [9] was on NH_4N_3 vapor, whereas Luft's [10] measurement over the higher temperature range was on NH_3 and HN_3 vapor.

Isothermal sublimation kinetics

No previous work has been done on the kinetics of the sublimation of ammonium azide. In view of the possible gas-phase secondary reaction its kinetics are best studied using weight-loss measurements. In the weighing chamber dry argon was continuously passed at a flow rate of 1.7×10^{-4} l s^{-1} to prevent the condensation of the vapor on the weighing pan. The sublimation curve is depicted in a plot of fractional sublimation, $\alpha(t)$ (where $\alpha(t)$ is the ratio of the weight loss at time t, $\Delta w(t)$, to the weight, w_0, of the sample), versus time t. Figure 3 shows a typical sublimation curve at 360 K. The curve is linear throughout the entire course of the reaction. This linear

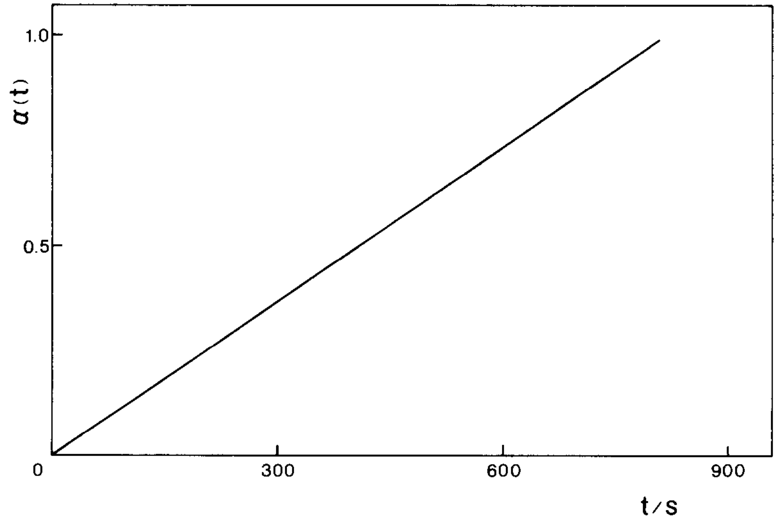

Fig. 3. Isothermal sublimation curve at 360 K.

kinetics was also observed in the sublimation of all four halides [13]. However, in ammonium perchlorate, the kinetics follow a contracting-volume equation $1-(1-\alpha)^{1/3}=kt$ or a contracting-surface equation $1-(1-\alpha)^{1/2}=kt$ depending on the temperature range. A linear kinetics implies that there is always a constant concentration of molecules at the reaction sites so that the rate is constant (zero-order reaction).

$$\frac{d\alpha}{dt}=k \tag{7}$$

From the Arrhenius plot, an activation energy of 93.7 kJ mol^{-1} and a frequency factor of 4.8×10^{11} s^{-1} were deduced over the temperature range 360–389 K. The Jacobs and Kureishy method [15] was also used to abstract the energy parameter and the value obtained for E of 92.8 kJ mol^{-1} is in excellent agreement with that obtained from the rate constant (see Table 2). This gives an average E value of 93.3 kJ mol^{-1}.

Jacobs and Russell-Jones [12] made a comprehensive theoretical study of ammonium perchlorate based on a model of dissociative sublimation and suggested that its activation energy should be about one-half its heat of sublimation. This was indeed confirmed by their experimental results. In the case of the ammonium halides, the values of E were unusually low, about one-third their respective values of ΔH_{sub}. Schultz and Dekker [16] derived the rate constant for the sublimation of NH_4Cl assuming the crystal surface was fully covered by an adsorbed layer of an $NH_3\cdots HCl$ complex and that the step corresponding to step 5 in eqn. (3) was the rate-determining step. The experimental value of E and the frequency factor, A, agreed fairly well with their estimated values. Chaiken et al. [13] extended the measurements to other halides and confirmed that the Schultz and Dekker mechanism for sublimation was also observed by the other halides, including fluoride which exhibits H-bonding in the solid state.

In the present study on NH_4N_3, sublimation does not proceed via a dissociation mechanism as has been fully discussed above. The activation energy of 93.3 kJ mol^{-1} is slightly larger than its sublimation enthalpy, ΔH_{sub} (73.6 kJ mol^{-1}). Linear kinetics and approximately equal values between E and ΔH_{sub} are generally observed for monatomic metal and

TABLE 2

Kinetics parameters from isothermal TG

Temperature, T(K)	Rate constant 10^2k (s^{-1})	E (kJ mol^{-1})	A (s^{-1})
359.7	13.7	93.7 [a]	4.8×10^{11}
372.2	6.6	92.8 [b]	–
382.2	4.1		
388.5	1.2		

[a] by rate constant method.

[b] by Jacobs–Kureishy method.

monomolecular solids such as pentaerythritol tetranitrate [17]. Thus it appears that NH_4N_3 vapor exists in monomeric form.

CONCLUSION

Ammonium azide is thermally unstable and undergoes molecular sublimation. The DSC thermogram shows that it is endothermic (73.4 kJ mol^{-1}) and its vapor readily dissociates into ammonia and hydrazoic acid. This dissociation is accompanied by a heat of reaction of only 67.7 kJ mol^{-1}. However, no decomposition of these gases was observed up to the temperature of 513 K. Upon cooling the reverse processes took place in a stepwise manner. The gases first recombined in the vapor phase followed by the subsequent condensation of the NH_4N_3 vapor into the solid state. The sublimation kinetics are of zero-order, with an activation energy, E, of 93.3 kJ mol^{-1} over the temperature range 360–389 K. This value is larger but of similar magnitude to its heat of sublimation. It is suggested that its vapor exists in monomeric form before dissociation.

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