

LOW/HIGH TEMPERATURE RELATIONSHIPS IN DINITRAMIDE SALTS BY DEA/DSC AND STUDY OF OXIDATION OF ALUMINUM POWDERS BY DSC/TG

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Abstract

The dinitramide salts of ammonia (ADN), hexamethylenetetramine (HDN), potassium (KDN), and sodium (NaDN) showed a linear relationship between the DSC rate of decomposition at the peak maximum and the DEA $\tan\delta$ value at the low temperature transition peak. As the cation basicity increased in the series $ADN < HDN < KDN \leq NaDN$, there was an increase in the low temperature transition peak, the energy barrier for relaxation, and the decomposition peak temperature, and a decrease in the $\tan\delta$ value at the low temperature transition peak, specific heat capacity, and the rate and enthalpy of decomposition. The more basic salts were more thermally stable (i.e., higher decomposition temperature) and less energetic (i.e., lower enthalpy of decomposition). The more internal free volume (disorder) present in these salts, the higher the rates of relaxation and decomposition. Five aluminum powders of different surface areas were analyzed by DSC in platinum sample pans, and it was found that the enthalpy and rate of oxidation increased as the particle size of Al decreased while the enthalpy of the Al melt decreased. TG showed a two-step weight gain in the oxidation of Al with plateaus in the 650 and 1130°C regions and the percent weight gain increased as the particle size of Al decreased. Variable DSC and TG heating rate studies showed that the activation energies for the first step in the oxidation process increased as the particle size of Al increased.

Keywords: basicity, dinitramides, kinetics, oxidation, $\tan\delta$, transition temperatures

Introduction

Dinitramide salts are a promising new class of energetic oxidizers for use in propellants and explosives [1]. Aluminum powders have long been used as fuels in underwater explosives. These two unrelated materials for explosives are investigated in this paper. In this study low temperature transitions in dinitramide salts of ammonia, hexamethylenetetramine, potassium and sodium were investigated by dielectric analysis (DEA) and modulated differential scanning calorimetry (MDSC), and high temperature decomposition by differential scanning calorimetry (DSC). The effects of particle size (surface area) on the enthalpies of oxidation and melting and weight gain for five aluminum powders with mean particle sizes ranging from 0.1 to 20 microns were studied by DSC and thermogravimetry (TG).

Experimental

DEA, DSC and TG experiments were carried out on TA Instruments models 2970 DEA, 2910 DSC, 2950 TGA with models 2100 and 3100 Thermal Analysts. In DEA, a 100 ± 10 mg sample was spread out on the single surface sensors and a force of 10 Newtons was applied. The samples were heated to the melting point (95 to 135°C) of the salts at 2°C min^{-1} , cooled at 2°C min^{-1} to -100°C and then reheated at 2°C min^{-1} to 100°C . Several frequencies were employed and data obtained at 10, 100 and 1000 Hz during the second heating step are reported. Low temperature MDSC runs were carried out with a refrigerated cooling accessory (RCA) from the melt to -70°C at 2°C min^{-1} in a helium atmosphere with the samples (about 10 mg) enclosed in crimped Al pans. MDSC experiments were calibrated with indium, sapphire, and polystyrene standards. DSC and TG oxidation experiments of Al were run in platinum sample pans containing 4–5 mg of sample at 5°C min^{-1} in static air to 700 and 1130°C respectively.

Discussion

Dinitramide salts

Ammonium, potassium, and sodium salts of dinitramide are labeled as ADN, KDN, and NaDN respectively while hexamethylenetetramine dinitramide is HDN. Two HDN salts were analyzed [2], one was recrystallized from methanol with a density of 1.60 and was triclinic while the other was from water with a density of 1.64 and was monoclinic. These two HDN samples were readily distinguishable by their DEA $\tan\delta$ peak shapes and peak temperatures. However only the results for HDN from methanol are reported. Figure 1 shows $\tan\delta$ (ratio of conductance to capacitance) curves at a frequency of 1 kHz. The peaks may be due to steric hindrance about the $(\text{NO}_2)\text{N}(\text{NO}_2)$ group. HDN had a pronounced shoulder which indicated additional relaxation processes. The frequency dependence of the $\tan\delta$ peaks are presented in Table 1. As the frequency increased, the peaks shifted to higher temperatures. Activation energies for the relaxation process may be calculated from the slope of a plot of log applied frequencies vs. the reciprocal of the absolute peak

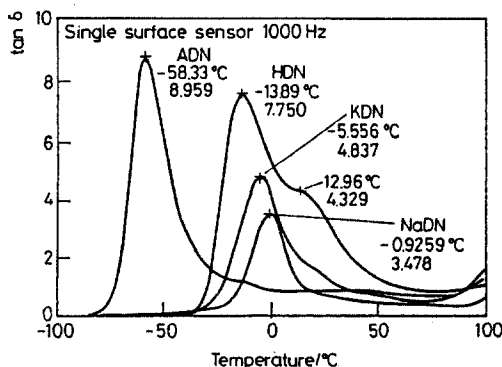


Fig. 1 DEA $\tan\delta$ plots for dinitramide salts at 1 kHz

Table 1 DEA data for dinitramide salts

Sample	tan δ °C			tan δ at T_g 1000 Hz	E_a kJ mol $^{-1}$
	10 Hz	100 Hz	1000 Hz		
ADN	-75	-68	-58	9.0	96
HDN	-31	-24	-14	7.8	142
KDN	-23	-18	-6	4.8	205
NaDN	-19	-10	-1	3.5	302

temperatures; straight line plots were obtained. The kinetic data are also reported in Table 1 along with tan δ values (ϵ''/ϵ') at the peak temperatures. It was found that the tan δ peak temperatures and activation energies were in the order ADN<HDN<KDN<NaDN. The tan δ peak values (ϵ''/ϵ') were in the order ADN>HDN>KDN>NaDN. In this series the loss factor (ϵ'') values are much greater than the permittivity values (ϵ'). Consequently tan δ values are dominated by the loss factor. ADN had the highest tan δ value which meant it had the highest mobility for internal rotation of the dinitramide group, therefore it had the lowest transition temperature and the lowest energy barrier for rotation. The order of cation basicity is NaDN \geq KDN>HDN>ADN. Based on electronegativity values potassium (0.8) should be slightly more basic than sodium (0.9). However in this study it appeared that the sodium salt was slightly more basic. An increase in basicity (i.e., ionicity) imposed a greater degree of order on the dinitramide group, i.e., it had less freedom of movement as shown by a decrease in tan δ , consequently its transition temperature was higher because it needed more thermal energy for relaxation and its energy barrier was likewise higher. The trends in the DEA data may be explained on the basis of order-disorder relationship. The more order present in the salt as measured by the cation basicity then the higher the transition temperature and activation energy for the relaxation process. While the more disorder present as measured by the loss factor or tan δ then the lower the transition temperature and energy barrier.

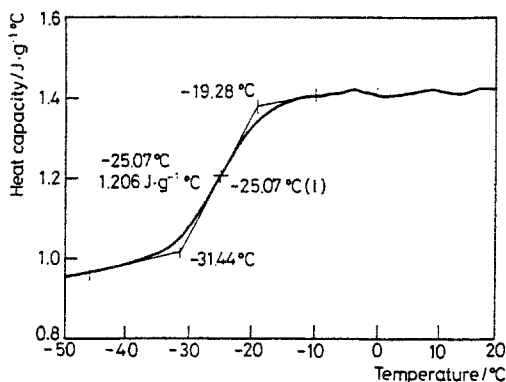
**Fig. 2** MDSC C_p curve for HDN

Table 2 MDSC and DSC data for dinitramide salts

Sample	MDSC		DSC		
	$T_g^{(1)}$ °C	$C_p^{(2)}$ at T_g J (g °C) ⁻¹	$T_d^{(3)}$ peak/ °C	Rate ⁽⁴⁾ / W g ⁻¹	Enthalpy ⁽⁵⁾ / J g ⁻¹
ADN	-47	1.3	180	5.6	2508
HDN	-25	1.2	203	4.7	1731
KDN	-5	0.7	220, 230 ⁽⁶⁾	1.6	652
NaDN	2	0.9	212, 162 ⁽⁶⁾	0.9	574

(1) T_g , glass transition temperature, °C

(2) C_p , specific heat capacity, J (g °C)⁻¹

(3) T_d , decomposition peak temperature, °C

(4) Rate, decomposition rate at peak maximum, W g⁻¹

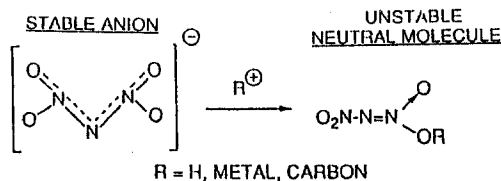
(5) Enthalpy, exothermic heat of decomposition, J g⁻¹

(6) Minor decomposition peak, °C.

Low temperature transitions in dinitramide salts were also observed by MDSC as shown by a typical specific heat capacity plot in Fig. 2. Transition temperature data presented in Table 2 paralleled the order found by DEA. Specific heat capacity data at the T_g , i.e. inflection point in Fig. 2 inversely paralleled the transition temperatures. An increase in heat capacity is accompanied by an increase in internal free volume [3] and disorder. MDSC data agreed with DEA data. An increase in cation basicity leads to an increase in order (i.e., decrease in $\tan\delta$), a decrease in free volume (i.e., decrease in C_p), and an increase in transition temperature as measured by $\tan\delta$ peak temperature and temperature at C_p inflection point.

High temperature thermal decomposition data obtained at 5°C min⁻¹ in air are given in Table 2. A typical plot is shown for ADN in Fig. 3. The decomposition temperature appeared to increase with increasing cation basicity while the reaction rate (W g⁻¹) at the peak maximum and enthalpy of decomposition (J g⁻¹) decreased. Thus more basic salts were more thermally stable and less energetic. Figure 4 shows a linear plot of DSC rate of decomposition at the peak maximum vs. DEA $\tan\delta$ value at the low temperature transition peak. Apparently the more internal freedom (disorder) present in these salts, the higher the rates of relaxation and decomposition.

Pak [4] observed a linear relationship between cation electronegativity and the rate constant for decomposition of dinitramide salts. Thermal decomposition of ADN yields ammonia and dinitramidic acid (HN₃O₄). Tartakovsky [5] reported that HN₃O₄ is a stronger acid than sulfuric, it is unstable and produces N₂O and HNO₃. Koppes [6] reported that the dinitramide salt which may be represented as:



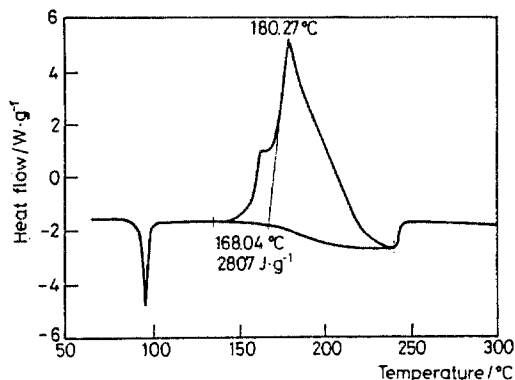


Fig. 3 DSC decomposition curve for ADN

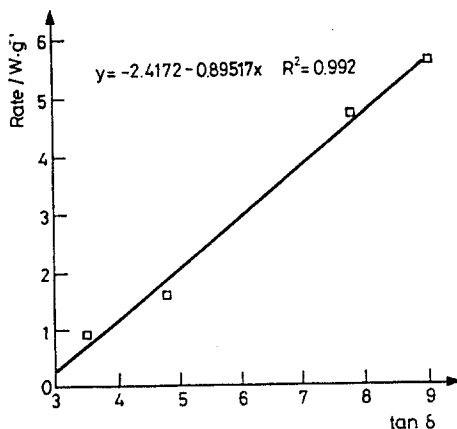


Fig. 4 DSC rate of decomposition at the peak vs. DEA $\tan\delta$ at transition temperature peak

is a stable anion which becomes unstable if converted to a neutral molecule. Therefore it is not unexpected that the stability of the dinitramide salt may increase as the basicity of the cation increases.

Aluminum powders

Five aluminum powders were examined. In order of increasing mean particle size they were labeled Alex (exploded aluminum, $\sim 0.1 \mu$), German ($\sim 0.9 \mu$), H-3 (3μ), H-12 (12μ), and MDX-81 (20μ). TG curves in static air at $5^{\circ}\text{C min}^{-1}$ for Alex and MDX-81 samples in platinum sample pans are shown in Fig. 5 from 400 to 1130°C . They revealed a two-step mass gain with a plateau in the 650°C region (solid state) followed by a rapid rise in mass gain (liquid state) with a leveling-off in the 1130°C region. Table 3 shows the percent mass gain by 1130°C . The oxidation of aluminum may be represented by the equation $4\text{Al} + 3\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3$ with a

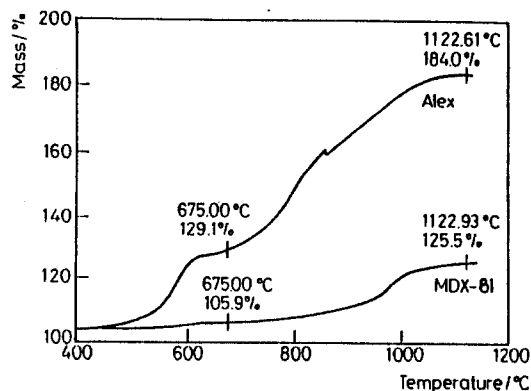


Fig. 5 TG oxidation curves for Alex and MDX-81 in air at $5^{\circ}\text{C min}^{-1}$

Table 3 TG oxidation data⁽¹⁾ for aluminum powders in platinum pans at $5^{\circ}\text{C min}^{-1}$ in air

Aluminum	% Mass gain at/ $\sim 1130^{\circ}\text{C}$	Particle size/ microns
Alex	84	~ 0.1
German	62	~ 0.9
H-3	57	3
H-12	25	12
MDX-81	25	20

⁽¹⁾ Data are the average of two runs

calculated percent mass gain of 89%. In this series of aluminum samples the percent mass gain increased as the mean particle size decreased i.e. 25% at 12 μ (H-12) to 84% at 0.1 μ (Alex). Thus as the surface area of aluminum increased there was a corresponding increase in mass gain due to oxidation. There weren't any differences by TG between particle sizes of 12 and 20 μ aluminum i.e. H-12 and MDX-81 respectively. The surface area of solid aluminum should lose its significance above its melting temperature (T_m), but apparently it hasn't as shown by the data in Table 3. Perhaps above T_m there isn't a single relatively large volume of liquid aluminum, but contiguous droplets of aluminum whose surface area is influenced by the surface area of the corresponding solid aluminum particles. On that basis, Alex would have a greater surface area in both the solid and liquid state in comparison to MDX-81. In addition, the diffusion of oxygen into the liquid aluminum would be expected to take place more readily and to a greater extent as the surface area of the thin layer of liquid aluminum increased. These assumptions could explain the data in Table 3. With solid aluminum there is a boundary layer of Al_2O_3 on the surface of Al which at elevated temperatures may crack/fracture/become porous and thereby permit the diffusion of oxygen into the core of Al. Alex and German Al have dark gray colors compared to the other Al samples, and at 1130°C these two samples have a white color due to the formation of Al_2O_3 . Examination of the Al_2O_3 showed that it was composed of fine particles without any lumps which

indicated that it may have been deposited from droplets. A TG variable heating rate oxidation study was carried out employing the method of Flynn and Wall [7] on the first oxidation step in Alex and MDX-81 in the 400 to 650°C region. These two samples were chosen because they are at the extreme ends of particle size/surface area in this series: Arrhenius plots were a straight line therefore an activation energy may be calculated from the slope of the line. Alex had a value of 264 kJ mol⁻¹ and MDX-81 had 369 kJ mol⁻¹ (Table 4). Thus the activation energy for the oxidation process correlated with the particle size of aluminum; as the particle size increased so did the activation energy for oxidation. Interestingly when the rates of oxidation for a first order reaction were calculated, the rates of reaction were the same for Alex and MDX-81 at 675°C namely 2×10² min⁻¹. When comparing two similar reactions (i.e. oxidation, decomposition, etc.) the one with a higher activation energy has a lower rate of reaction when the frequency factors (i.e. pre-exponential term) are invariant. However if an increase in activation energy is accompanied by a corresponding increase in the pre-exponential factor then the rates of reaction may be invariant, and this is an example of a kinetic compensation effect [8, 9]. This was observed in our study. A probable cause for this effect may be due to

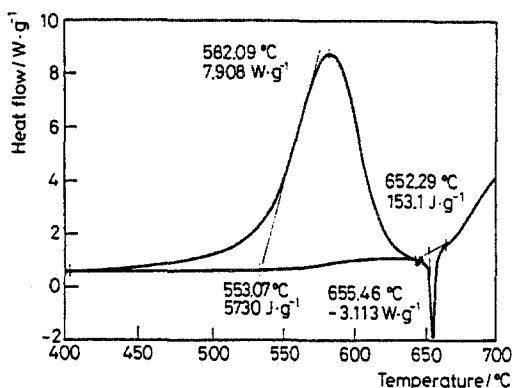


Fig. 6 DSC oxidation/melting curve for Alex in a platinum pan at 5°C min⁻¹

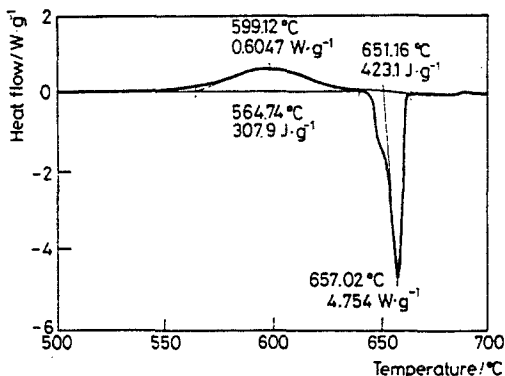


Fig. 7 DSC oxidation/melting curve for MDX-81 in a platinum pan in air at 5°C min⁻¹

Table 4 TG and DSC kinetic data for oxidation of aluminum in 400 to 650°C region

Aluminum	Activation energy/ kJ mol ⁻¹		Rate/min ⁻¹			
	TG	DSC	TG	DSC	TG	DSC
			675°C	675°C	500°C	500°C
Alex	264	243	2×10 ²	2×10 ²	1.7×10 ⁻¹	1.4×10 ⁻¹
MDX-81	369	394	2×10 ²	2×10 ²	5×10 ⁻³	4×10 ⁻³

an irreversible rate limiting process which requires some minimum temperature for initiation of bond breaking or formation [8].

DSC oxidation studies with these aluminum powders were carried out in platinum sample pans in static air at 5°C min⁻¹. Typical plots are shown for Alex and MDX-81 in Figs 6 and 7 in the 400 to 700°C region. They show a DSC exothermic oxidation peak followed by an endothermic melting peak. DSC data are summarized in Table 5. As the particle size of aluminum increases, the enthalpy (J g⁻¹) of oxidation decreases (Fig. 8), and the enthalpy of melting increases (Fig. 9). The trend in the melting region was expected because there is less free aluminum (i.e. unoxidized) present as the surface area increased because more aluminum has been oxidized, consequently there is less aluminum available for melting and the enthalpy of melting is less. A DSC variable heating rate kinetic study [10] was carried out on Alex and MDX-81 oxidation reactions.

The Arrhenius plots were straight lines which permitted the calculation of the activation energies for the processes. The values found were 243 kJ mol⁻¹ for Alex and 394 kJ mol⁻¹ for MDX-81 (Table 4). DSC and TG kinetic data were averaged to 254±15 kJ mol⁻¹ for Alex and 379±21 kJ mol⁻¹ for MDX-81. A kinetic compensation effect was also observed with the DSC activation energies and pre-exponential data. The DSC rates of reaction were similar to those found for the TG rates of reaction at 675°C. However if the rate constants were calculated for a temperature of 500°C then a kinetic compensation effect was not observed. The average value for the rate constant from DSC and TG data was 1.5×10⁻¹ min⁻¹ at 500°C for Alex and 4.5×10⁻³ min⁻¹ for MDX-81. The ratio of rate constants was ~30:1 (Alex:MDX-81)

Table 5 DSC oxidation data⁽¹⁾ for aluminum powders in platinum pans in 400–650°C region at 5°C min⁻¹ in air

Aluminum	ΔH / J g ⁻¹ oxidation	Rate/W g ⁻¹ oxidation	ΔH / J g ⁻¹ melting	Particle size/ microns
Alex	5747	7.93	146	~0.1
Genman	3030	4.41	270	~0.9
H-3	918	1.70	348	3
H-12	380	0.60	372	12
MDX-81	326	0.60	420	20

⁽¹⁾ Data are the average of two runs

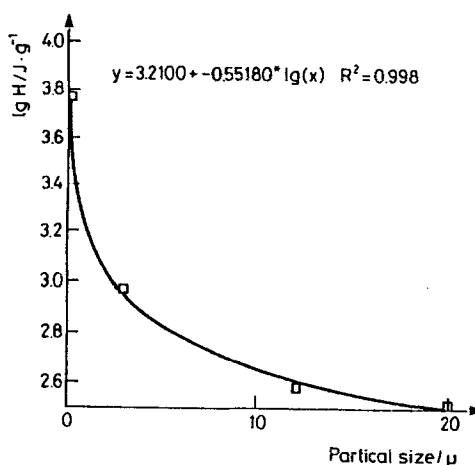


Fig. 8 DSC enthalpy of oxidation vs. particle size for aluminum powder

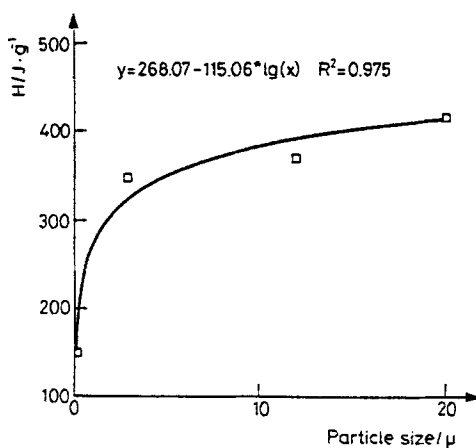


Fig. 9 DSC enthalpy of melt vs. particle size for aluminum powders

while the ratio of particle sizes was $\sim 200:1$ (MDX-81:Alex). Thus a 200-fold decrease in particle size was accompanied by a 30-fold increase in rate constant. The proportional increase in rate constant might be expected to be greater, i.e., proportional to the particle size ratio but it wasn't; perhaps because the diffusion of oxygen through successive layers of Al_2O_3 is the limiting factor.

Conclusion

In this series of dinitramide salts a linear relationship was observed between the DSC rate of decomposition at the peak maximum (high temperature reaction) and DEA $\tan \delta$ peak value at T_g (low temperature transition). An inverse relationship was found between the DEA activation energy for the low temperature relaxation

and the DSC enthalpy of decomposition. These results may be correlated with the change in basicity of the cation in this series. As the cation basicity increased in the order $ADN < HDN < KDN \leq NaDN$ the low temperature mobility as shown by $\tan \delta''/\epsilon'$ decreased, the internal free volume decreased as shown by C_p and the calculated energy barrier for relaxation increased. In terms of order – disorder increased basicity (i.e., ionicity) leads to an increase in order and a decrease in the rate and enthalpy of decomposition. The more basic salt is more thermally stable (i.e., higher decomposition temperature), it is less energetic (i.e., lower enthalpy) and has a lower rate of decomposition.

The magnitude of the oxidation reactions of the aluminum samples may be explained on the basis of surface area in both the solid and liquid state. As the surface area of solid aluminum increased, there was an increase in the enthalpy and rate of oxidation in the 400 to 650°C region, a decrease in the activation energy for oxidation, and a decrease in the enthalpy of melting. In the liquid state the presence of contiguous droplets instead of a single drop of aluminum would result in a larger liquid surface area which would enhance the diffusion of oxygen and the oxidation of aluminum in the melt and subsequent mass gain. As the surface area of solid aluminum increased, the surface area of the corresponding droplets of liquid aluminum would also be assumed to increase.

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The authors are grateful to Dr. William Koppes, Mr. Michael Sitzmann, and Mr. Rolf Renner for some of the samples used in this study.

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