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Thermal analysis of ammonium dinitramide (ADN)

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Abstract

Kinetic constants of decomposition were determined for ADN and prilled ADN by DSC and TG. Pressure DSC at 550 psi air or helium had similar kinetic constants for prilled ADN, namely 29 kcal/mol activation energy and a log frequency factor of $\sim$14.0 min^{-1}. These values were similar to those found in sealed sample pans in which the decomposition gases were confined. DSC and TG runs in open sample pans in nitrogen or helium had higher activation energies and frequency factors, namely 40–43 kcal/mol and 18–20 min^{-1}, respectively. Thus, it appears that confinement of the ADN decomposition gases either under pressurization or a sealed environment accelerates the decomposition of prilled ADN. Kinetics of decomposition of unprilled ADN at atmospheric pressure in nitrogen or helium by DSC and TG were E_a=37 kcal/mol and log A=17 min^{-1}. Unprilled ADN had lower activation energies and frequency factor for decomposition than prilled ADN which contained stabilizers. The effect of sample containment (i.e. aluminum, coated aluminum, gold, and glass ampoules) on the shape of the DSC curve of ADN was investigated. Isothermal TG in vacuum of ADN in the 45–75°C region and the DSC analysis of the TG residues showed unusual results in the 60°C region. The rate and enthalpy of decomposition of four dinitramide salts and their dielectric relaxation were related to the basicity of the cation. © 2000 Published by Elsevier Science B.V.

Keywords: Ammonium dinitramide; Prilled ADN; Kinetics of decomposition

1. Introduction

Ammonium Dinitramide [$NH_4N(NO_2)_2$] abbreviated ADN is a relatively new oxidizer which may be environmentally friendly because it does not have a halogen acid decomposition product. The decomposition reactions of ADN have been discussed by many researchers [1–3]. In the present study, the effect of sample pans, i.e. aluminum, coated aluminum, gold, and glass ampoule on the decomposition curve of ADN along with the effect of pressure and sealed sample pan will be discussed. Processing of ADN based propellant has been carried out under vacuum in the 60°C, region. Consequently, an isothermal TG study of ADN in vacuum (20–35 mm) was followed in the 45–75°C region. A DSC analysis of the TG residue was carried out. The TG/DSC curves were unusual. DSC and TG kinetic analyses of prilled/unprilled ADN under different experimental conditions were performed. Finally, a relationship was observed between the rate and enthalpy of decomposition of four dinitramide salts and their low temperature dielectric relaxation with the basicity of the cation.

2. Experimental

Three samples of ADN, namely prilled, unprilled NSWC Pilot Plant Lots 50-4, 50-6 and Lot K (recrys-

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tallized), and BOFORS (Department of Energetic Materials, Sweden) were investigated. DSC, TG, and DEA experiments were carried out on TA Instruments models 2910, 2950 and 2970, respectively with 2100 and 3100 thermal analysts. To test the precision of the DSC analysis five runs at 5°C/min in unsealed sample pans with a pin-hole in the cover were carried out and the peak temperature, rate, and enthalpy of the melting peak and decomposition peak were recorded for the different sample pans in a nitrogen atmosphere. Pressure DSC runs were made in a TA pressure DSC cell at 550 psi air and helium. Kinetic analyses were carried out employing a variable heating rate method [4].

3. Discussion

3.1. DSC sample pans

The DSC curve in Fig. 1 is for BOFORS ADN with the following thermal events, melting endotherm, decomposition exotherm, and sublimation endotherm due to ammonium nitrate [5]. With a coated (anodized) aluminum pan prilled ADN showed a doublet decomposition peak (Fig. 2). While in a gold pan the shape of the decomposition and sublimation peaks were different (Fig. 3). It was thought that the dissociation of ADN into ammonia and dinitramide acid (strong acid) may react with the regular aluminum sample pans. However, a reaction was only apparent with coated aluminum pans and possibly with gold pans. Ammonium nitrate (AN), a decomposition product of ADN showed an endothermic sublimation peak in 250°C region (Fig. 4) with regular Al pans and an exotherm peak in coated Al pans (Fig. 5). AN dissociates into ammonia and nitric acid (strong acid).

3.2. Sealed glass ampoules

In a sealed glass ampoule, prilled ADN displayed a much sharper exotherm peak (Fig. 6) with a three-fold increase in the reaction rate at the peak maximum

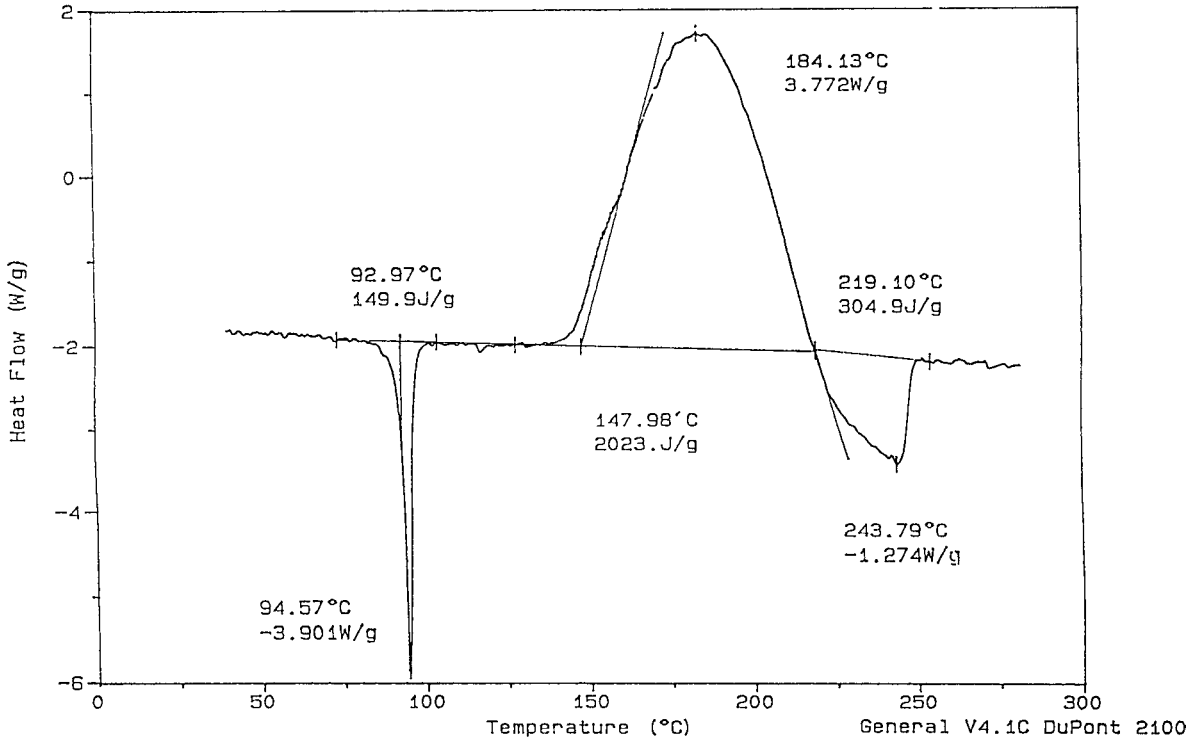

Fig. 1. DSC curve of BOFORS ADN in nitrogen at 5°C/min.

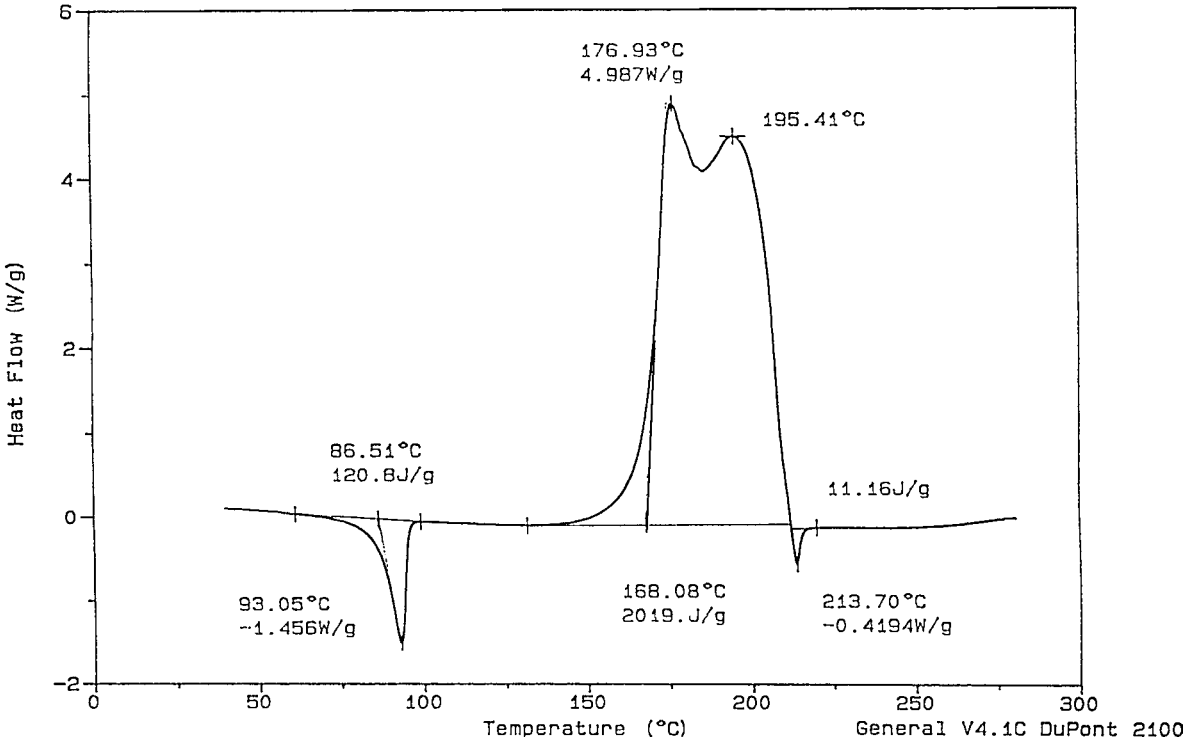

Fig. 2. DSC curve of prilled ADN in a coated Al pan in nitrogen at 5°C/min.

(11.2 vs. 4.5 W/g). Interestingly, a dark brown gas (NO_2) was observed in the ampoule when it was hot (~300°C) which turned colorless (N_2O_4) as the ampoule cooled. NSWC ADN Lot 50-6 was slightly broader than prilled ADN with a reaction rate only doubled (Fig. 7). BOFORS ADN in Fig. 8 was different from the other two and resembled more closely the decomposition exotherm in an aluminum pan (Fig. 1).

3.3. Pressure DSC

In an atmosphere of 550 psi air prilled ADN in Fig. 9 resembled prilled ADN in a sealed glass ampoule

Table 1
Prilled ADN in standard aluminum pans with pin-hole in cover at 5°C/min in nitrogen

Melt[a]			Decomposition[b]			Endotherm[c]	
Mass (mg)	Peak (°C)	Enthalpy (J/g)	Peak (°C)	Rate (J/g s)	Enthalpy (J/g)	Peak (°C)	Enthalpy (J/g)
1.37	92.8	124.5	182	4.51	1826	236	–
1.96	92.8	120.0	180	4.52	1884	243	289
2.37	93.2	118.3	179	4.61	1876	241	249
2.83	92.0	114.3	180	4.42	1873	250	288
3.10	92.5	115.6	–	4.62	1894	248	275

[a] Standard deviations: melt (°C): 92.7±0.4°C; melt (J/g): 118±4.
[b] Decomposition (°C): 180±1; decomposition (J/g s): 4.54±0.08; decomposition (J/g): 1871±26.
[c] Endotherm (°C): 244±5; endotherm (J/g): 275±19.

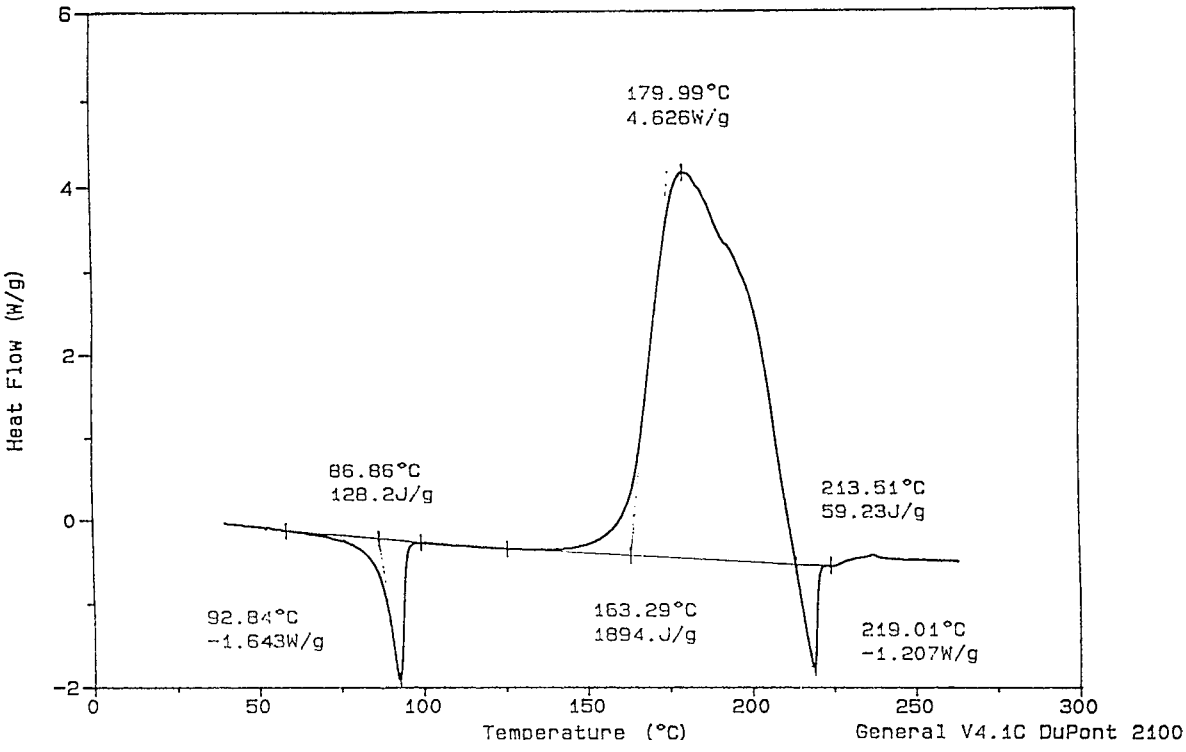

Fig. 3. DSC curve of prilled ADN in a gold pan in nitrogen at 5°C/min.

(Fig. 6) except its melting peak was slightly broader and it was shifted to a lower temperature (83°C). NSWC ADN Lot K in 550 psi air in Fig. 10 resembled an atmospheric run except the peak temperatures for melting and decomposition were shifted to a lower temperature, namely 86 and 167°C, respectively. Switching the atmosphere to 550 psi helium in Fig. 11 broadened and lowered the melting peak to 64°C and produced a broader decomposition peak with a pronounced high temperature shoulder at 179°C. In a vacuum (35 mm), the DSC curve of NSWC ADN Lot K in Fig. 12 again resembled that in an atmospheric run as far as peak temperatures for melting and decomposition were concerned but the enthalpy of decomposition was lowered from ∼1871 to 1315 J/g because of sublimation. Reproducibility of five ADN (prilled) runs are presented in Table 1 and the data showed good precision. The effect of sample containment on ADN (prilled) are given in Table 2 and the data were able to differentiate between the sample pans, i.e. aluminum, gold vs. coated aluminum vs. glass ampoule.

Table 2
Comparison of DSC data for prill ADN obtained in different sample containers in nitrogen at 5°C/min

Melt			Decomposition			
Sample pan	Peak (°C)	Enthalpy (J/g)	Peak #1 (°C)	Rate (J/g s)	Enthalpy (J/g)	Peak #2 (°C)
Aluminum	93	118	180	4.54	1871	
Coated Aluminum	93	126	179	5.08	2048	195
Gold	93	124	181	4.47	1836	
Glass ampoule	91	120	176	15.2	2126	

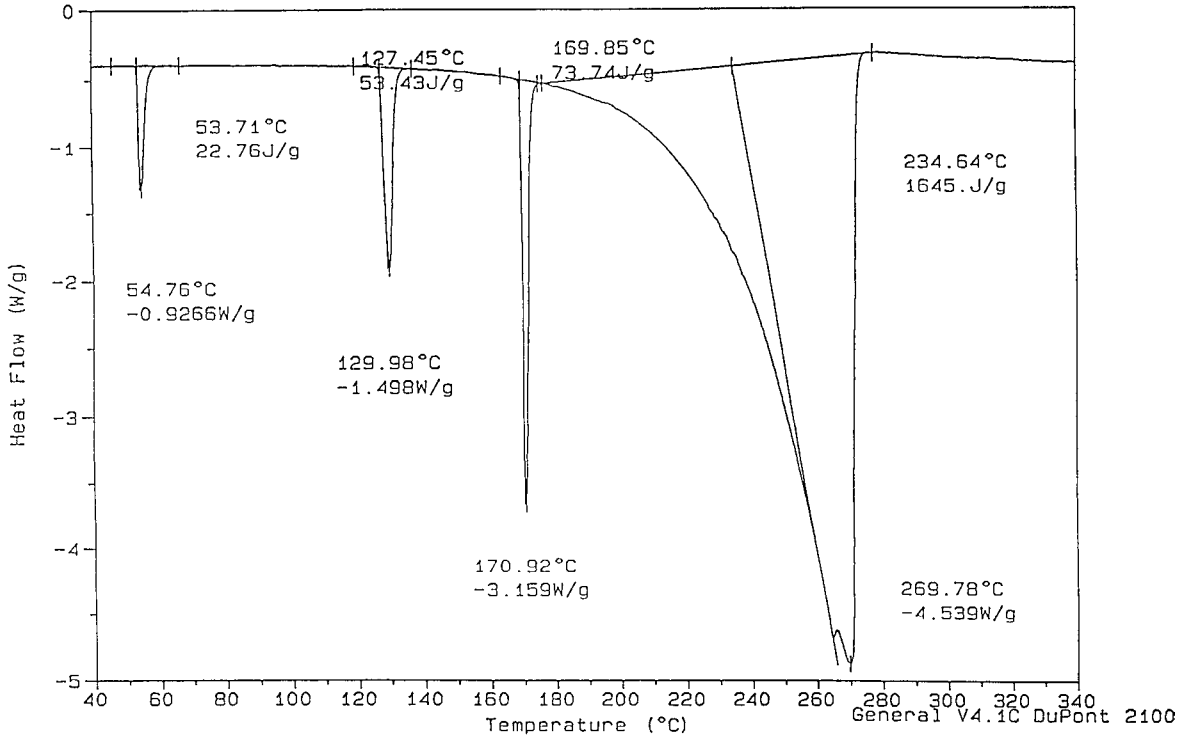

Fig. 4. DSC curve of AN in nitrogen at 5°C/min.

4. Isothermal TG

Isothermal TG curves in a vacuum of 20–35 mm for BOFORS at 52, 62, and 77°C revealed some unexpected results (Figs. 13–15). The percent weight loss was ∼26% after 1400–2500 min at 52 and 62°C but only ∼4% at 77°C. The experiments were repeated and the results were the same. Prilled ADN produced the same results as BOFORS. NSWC ADN Lot 50-4 was different (Fig. 16); its isothermal curve at 62°C only resulted in a 7% weight loss, but Lot 50-6 was similar to BOFORS ADN. The only differences between NSWC Lots 50-4 and 50-6 were particle size (i.e. small clumps vs. powder) and perhaps absorbed moisture (<0.5%). DSC runs were carried out on the isothermal TG residues at the different temperatures. Typical DSC curve for 52/62°C TG residue is presented in Fig. 17 and at 77°C in Fig. 18 for BOFORS ADN. Fig. 17 showed the presence of AN with an endotherm peak at 59°C which subsequently lowered the ADN melting peak from 94 to 83°C. However, the ADN exothermic decomposition peak temperature, rate, and enthalpy remained unchanged (compare to Fig. 1). Surprisingly, the DSC curve in Fig. 18 for the BOFORS TG residue at 77°C/1600 min did not show the presence of AN at 59°C and the curve was similar to untreated ADN in Fig. 1. Isothermal TG weight-loss data in vacuum are presented in Table 3 for prilled

Table 3
Isothermal TG weight loss rate data for prill ADN in vacuum (20 mm)

Temperature (°C)	Rate (10^{-2}%/min)	
	K_1 1st step	K_2 2nd step
40	0.05	0.2
45	0.3	1.9
50	0.5	4.3
55	3.4	2.0
60	8.6	2.7
65	4.5	1.4
70	0.5	0.2
75	0.7	0.3

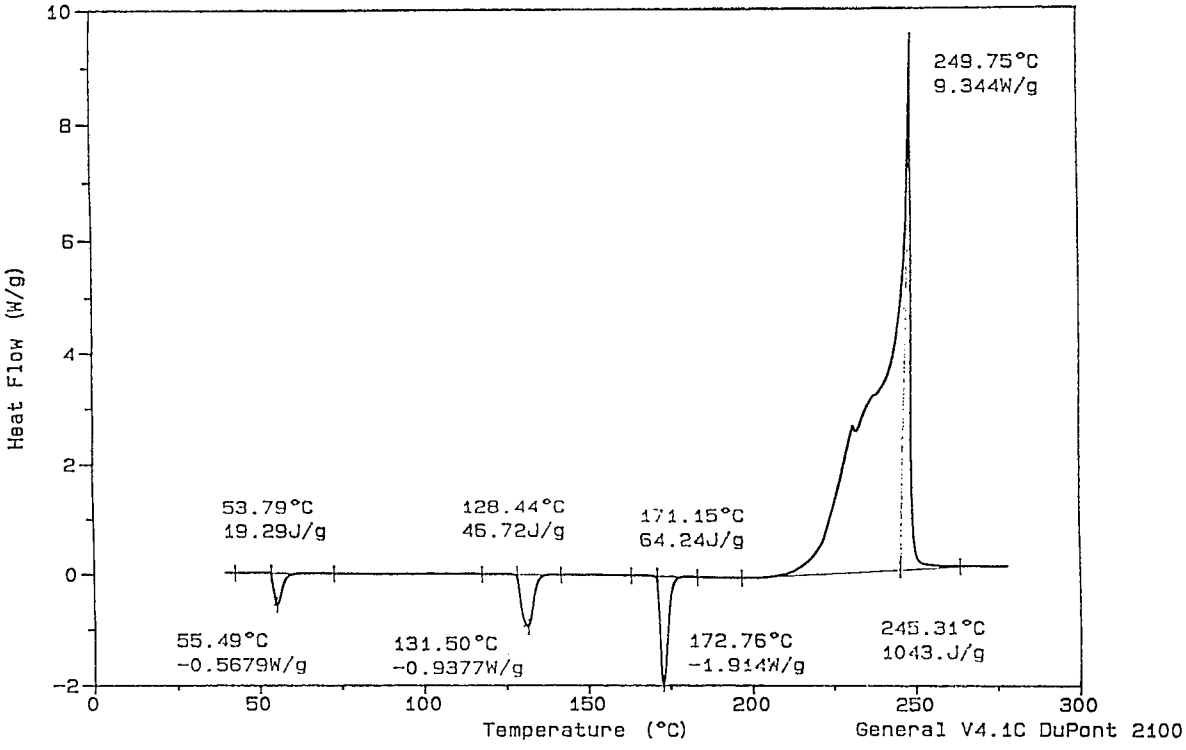

Fig. 5. DSC curve of AN in coated Al pans in nitrogen at 5°C/min.

ADN. It showed that the rate increased in the 50–65°C, region with a maximum in the 60°C region. Russell [1] found that ADN-An formed a eutectic in this temperature range; Manelius [6] observed a behavioral change in this region; Tompa et al. [7] reported a rate change by microcalorimetry in this range. Thus, isothermal heating in vacuum of ADN at temperatures in the region of the AN phase transition at 59°C favors the formation of AN in ADN, while at temperatures ca. 10°C higher do not. Since ADN exothermic decomposition peak temperature, rate and enthalpy of reaction were apparently unaffected by treatment in both temperature regions, the phenomenon may be due to sublimation and not decomposition. Observation of behavioral change in 60°C region were also found by MDSC dynamic heat capacity measurements of NSWC ADN Lot 50-6 which showed a small plateau in this region (Fig. 19); and a TMA expansion curve (Fig. 20) which showed probe penetration in this region.

4.1. Kinetics

Typical DSC Arrhenius plot for ADN is presented in Fig. 21 and by TG in Fig. 22. The TG plots showed slope changes with extent of conversions; activation energies decreased as the extent of conversion increased which was in agreement with that reported by Vyazovkin [3]. DSC and TG kinetic data are reported in Tables 4 and 5 for prilled and unprilled ADN. Pressure DSC at 550 psi air or helium had similar kinetic constants for prilled ADN, namely 29 kcal/mol (122 kJ/mol) activation energy and a log frequency factor of $\sim$14.0 min^{-1}. These values were similar to those found in sealed sample pans in which the decomposition gases were confined. Kinetic runs for prilled ADN in open sample pans in nitrogen or helium had higher activation energies and frequency factors, namely 40–42 kcal/mol (168–176 kJ/mol) and 18–20 min^{-1}, respectively. Thus, its appeared that confinement of the ADN decomposi-

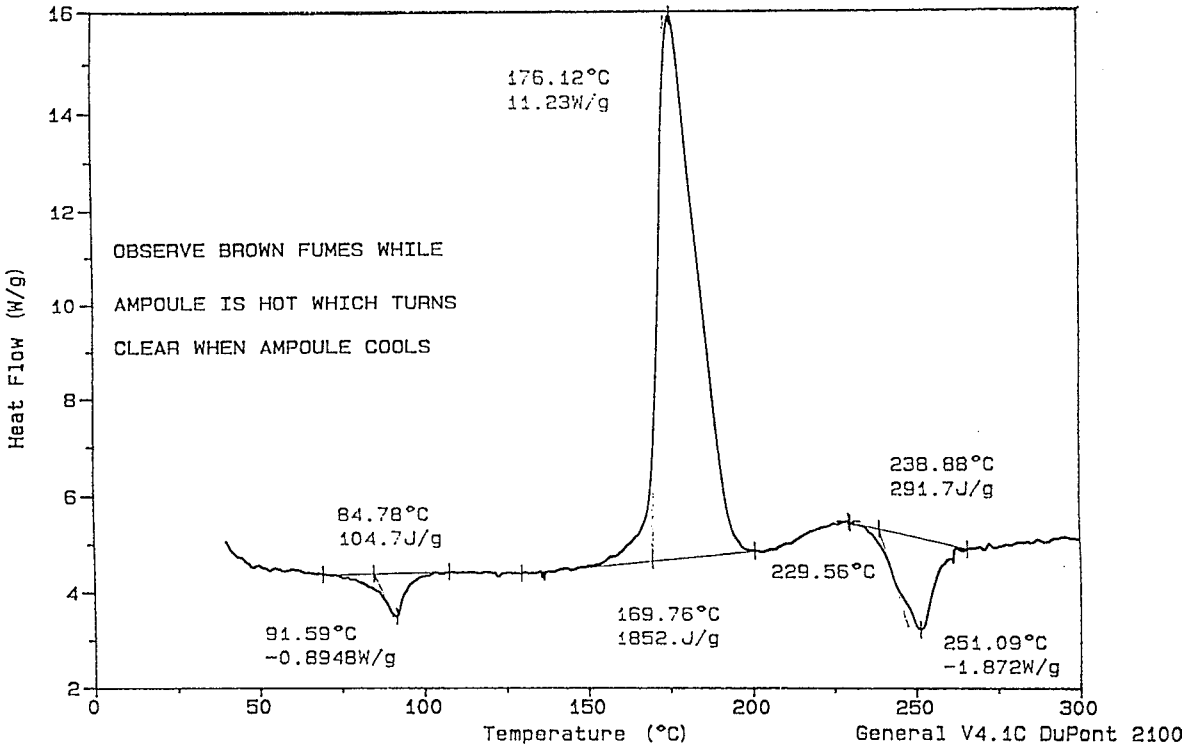

Fig. 6. DSC curve of prilled ADN in sealed glass ampoule at 5°C/min.

tion gases either under pressurization or a sealed environment accelerated the decomposition reaction. Kinetic of decomposition of NSWC and BOFORS ADN in nitrogen or helium by DSC were 36–38 kcal/mol (151–159 kJ/mol) and log A of 17–18 min^{-1}. In a vacuum of 35 mm, the DSC kinetic constants for

Table 4
DSC and TG kinetic data for prilled/unprilled ADN

ADN	Method	E_a (kcal/ml)	Log A (min^{-1})
1. Prill	PDSC, 550 psi air	29.3	13.92
	PDSC, 550 psi He	29.5	14.22
	DSC, N_2	41.9	19.97
	DSC, He	43.1	20.32
	DSC, sealed pan	30.8	14.67
	TG, He	40.2	18.67
2. NSWC LOT K	DSC, N_2	36.8	17.31
	TG, He	37.9	17.62
3. NSWC LOT 50-6	DSC, N_2	38.6	18.00
	DSC, vacuum (35 mm)	31.2	14.42
	DSC, glass ampoule	20.9	11.47
	TG, N_2	43.2	20.64
Aged in TG 25 mm vacuum at 56°C/2500 min	DSC, N_2	39.1	18.38

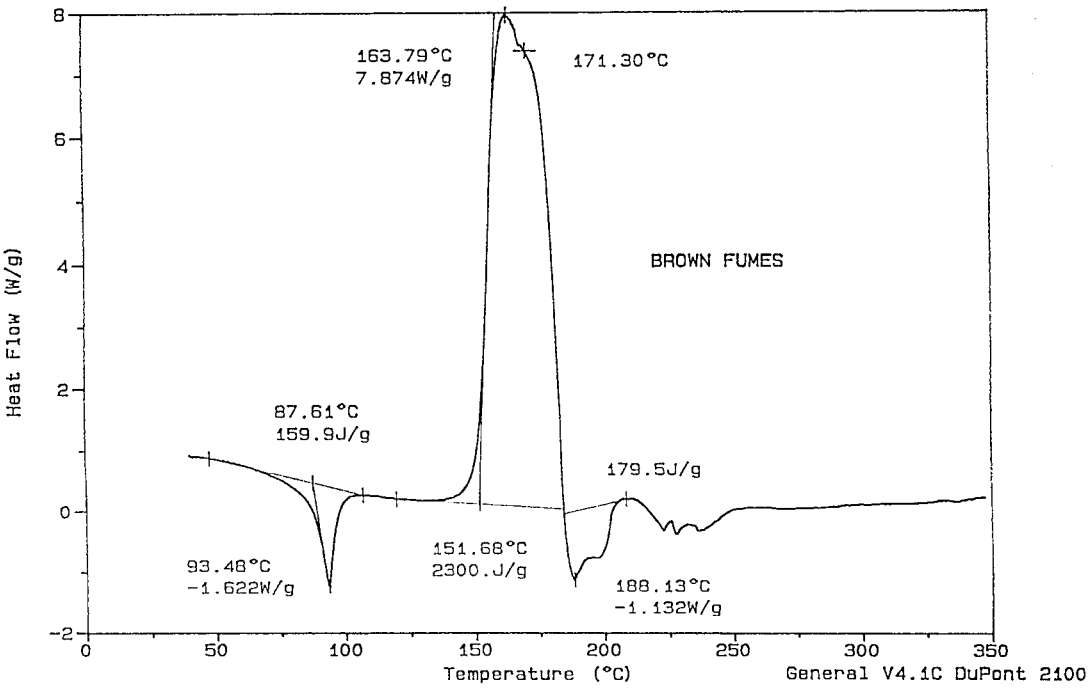

Fig. 7. DSC curve of NSWC ADN Lot 50-6 in a sealed glass ampoule at 5°C/min.

Table 5
DSC/TG dynamic kinetic data for BOFORS ADN

	DSC[a]	DSC[b]	TG[c]
E_a (kJ/mol)	161	89	168
E_a (kcal/mol)	38	21	40
Log A (min^{-1})	18.89	9.80	19.32

[a] DSC in unsealed pan with pin-hole in cover in nitrogen flow.
[b] DSC in sealed glass ampoule.
[c] TG in nitrogen flow.

unprilled NSWC ADN was similar to those for confined/pressurization prilled ADN. The lowest value for decomposition kinetics were found for NSWC/BOFORS ADN in sealed glass ampoules. Dark brown gas (NO_2) was visible in the free air space in the heated ampoule which turned colorless (N_2O_4) as the ampoule cooled. Prilled ADN which contained a stabilizer had higher activation energy and frequency factor than unprilled ADN in nitrogen/helium.

Table 6
MDSC and DSC data for dinitramide salts

Sample	MDSC			DSC	
	T_r (°C)[a]	C_p[b] at TG	T_d[c] Peak	Rate (W/g)[d]	Enthalpy (J/g)[e]
AND	−47	1.3	180	5.6	2508
HDN	−25	1.2	203	4.7	1731
KDN	−5	0.7	220, 230[f]	1.6	652
NaDN	2	0.9	212, 162[f]	0.9	574

[a] Relaxation transition temperature (°C).
[b] Specific heat capacity (J/g °C).
[c] Decomposition peak temperature (°C).
[d] Rate, decomposition rate at peak maximum (W/g).
[e] Enthalpy, exothermic heat of decomposition (J/g).
[f] Minor decomposition peak (°C).

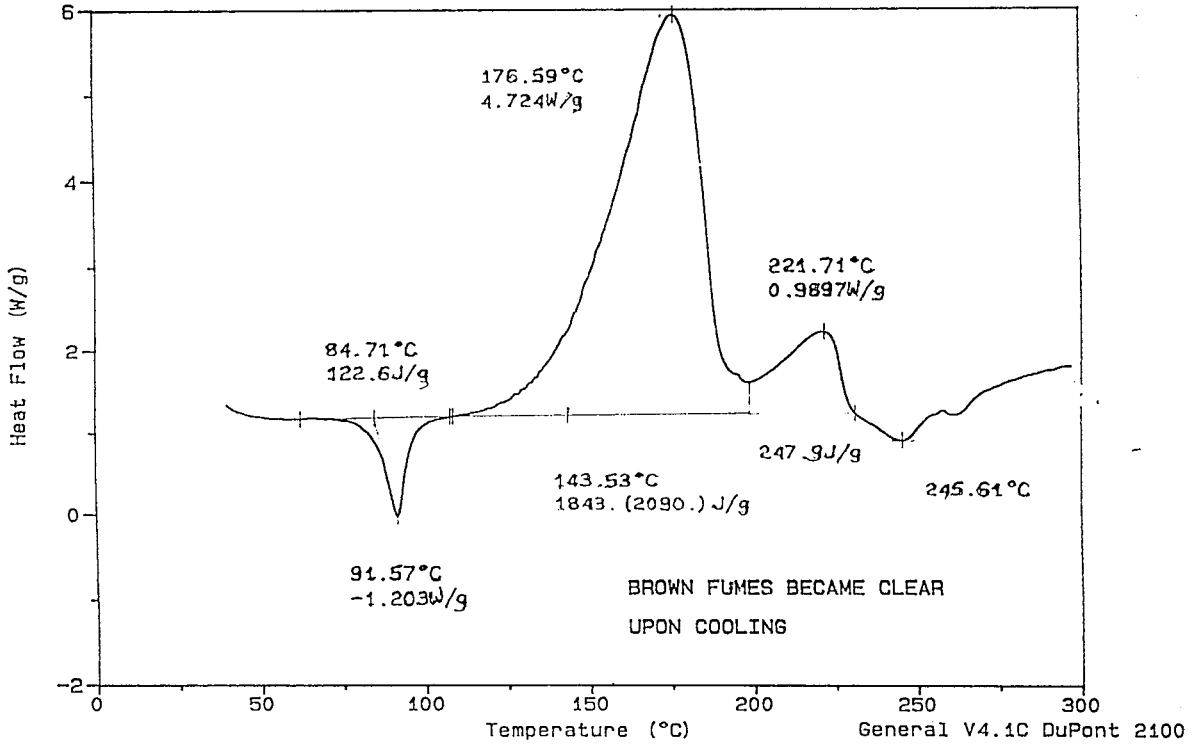

Fig. 8. DSC curve of BOFORS ADN in a sealed glass ampoule at 5°C/min.

4.2. Dinitramide salts

The dinitramide salts of ammonia (ADN), hexamethylenetetramine (HDN), potassium (KDN), and sodium (NaDN) were investigated by Tompa [8]. He found that the rate and enthalpy of decomposition decreased as the cation basicity increased (Table 6) and that the dielectric relaxation peak temperature and activation energy for relaxation increased as the cation basicity increased (Table 7).

5. Conclusions

Kinetic constants of decomposition were determined for ADN and prilled ADN by DSC and TG. Pressure DSC at 550 psi air or helium had similar kinetic constants for prilled ADN, namely 29 kcal/mol activation energy and a log frequency factor of $\sim$14.0 min^{-1}. These values were similar to those found in sealed sample pans in which the decomposition gases were confined. DSC and TG runs in open

Table 7
DEA data for dinitramide salts

Sample	Tan δ			Tan δ at	E_a (kJ/mol)
	(°C)			T_r	
	10 Hz	100 Hz	1000 Hz	1000 Hz	
AND	−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

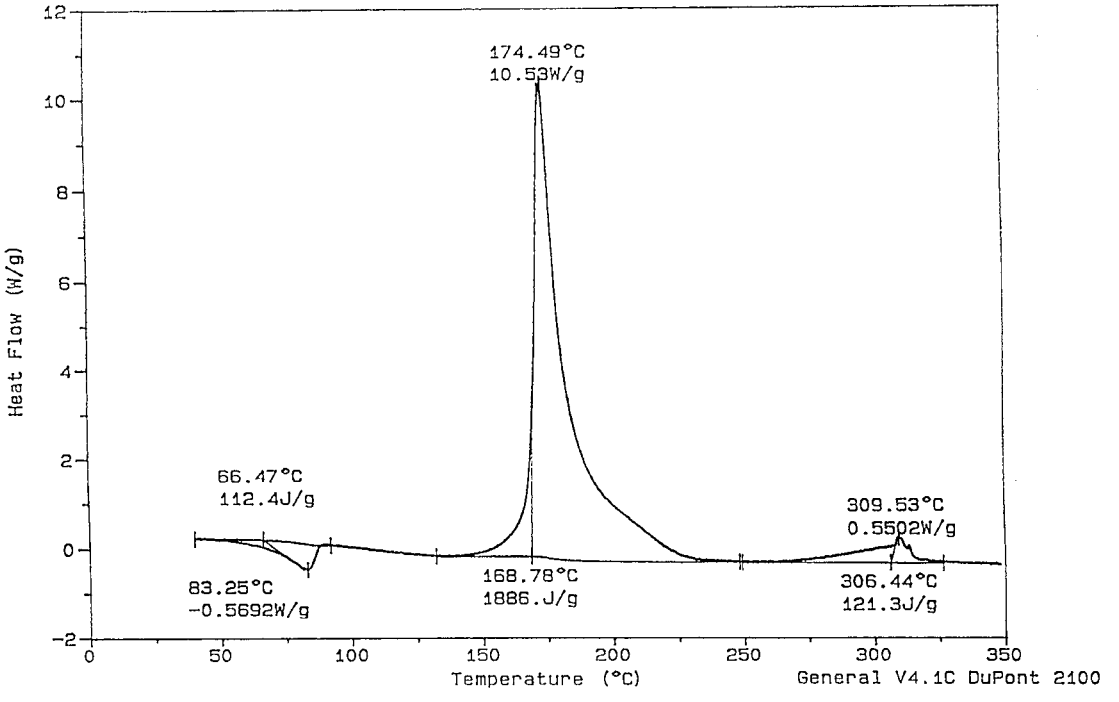

Fig. 9. PDSC curve of prilled ADN in 500 psi air at 5°C/min.

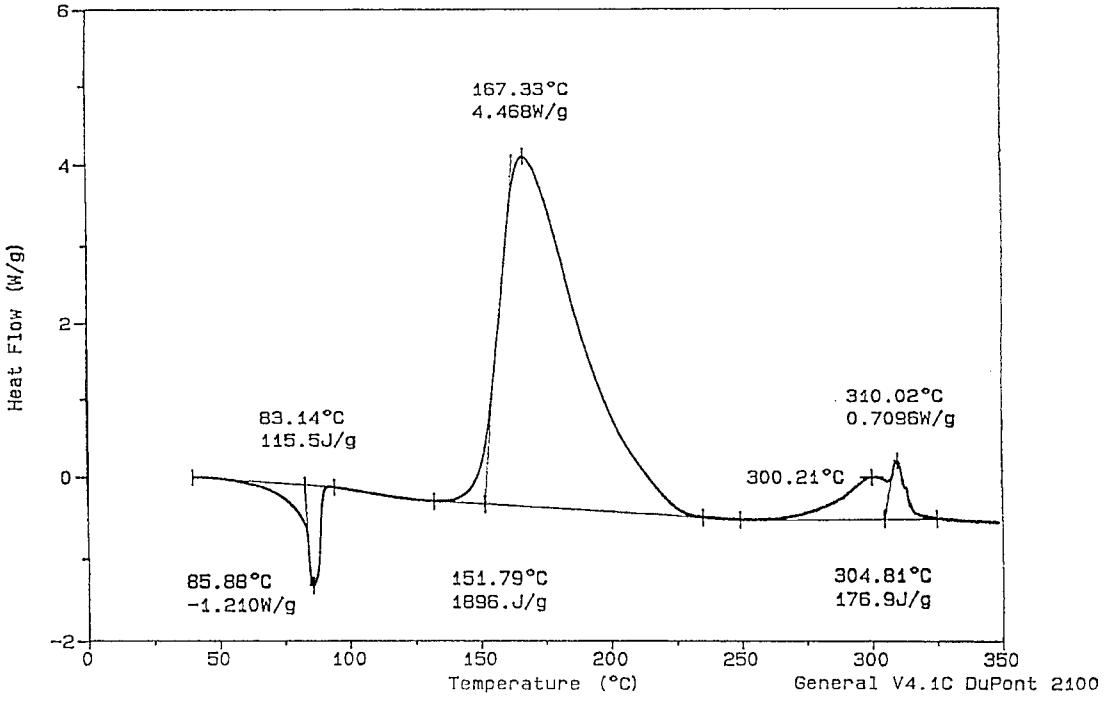

Fig. 10. PDSC curve of NSWC ADN lot K in 550 psi air at 5°C/min.

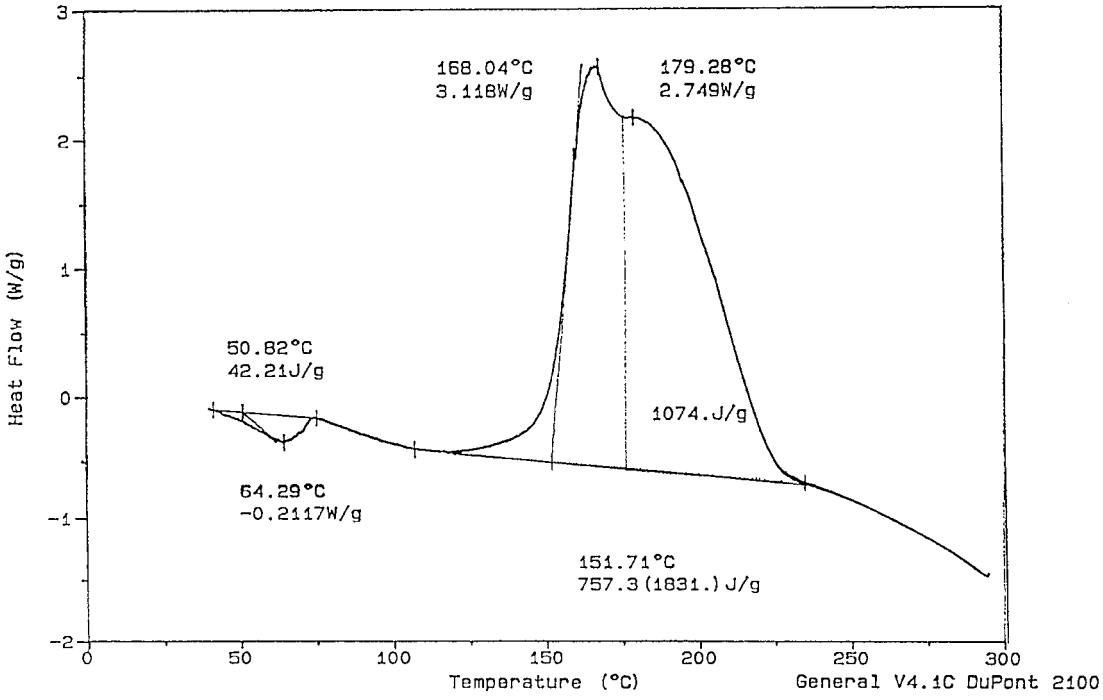

Fig. 11. PDSC curve of NSWC ADN lot K in 550 psi helium at 5°C/min.

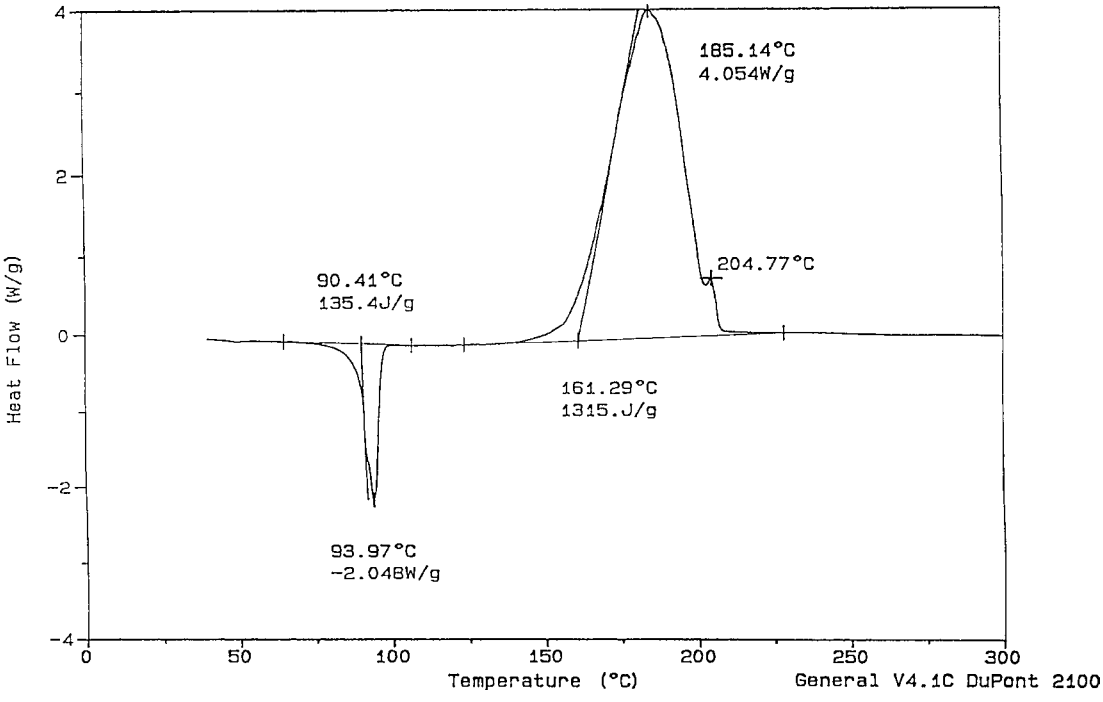

Fig. 12. DSC curve of NSWC ADN lot 50-6 35 mm vacuum at 5°C/min.

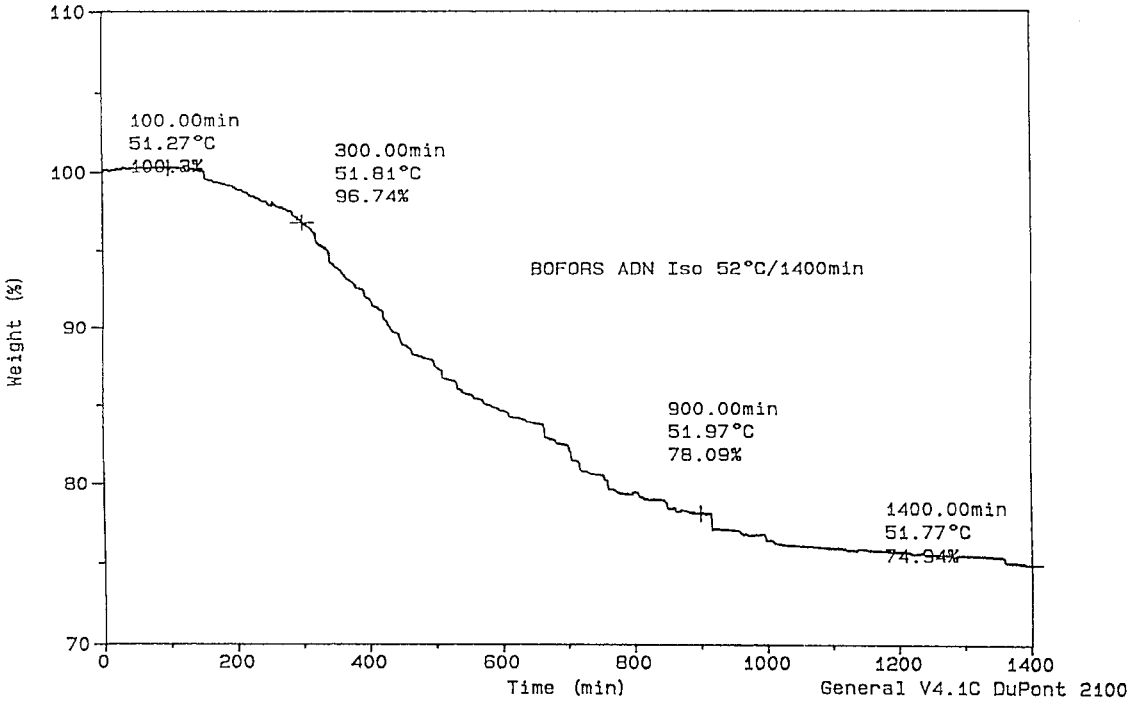

Fig. 13. Isothermal TG curve of BOFORS ADN in 35 mm vacuum at 52°C.

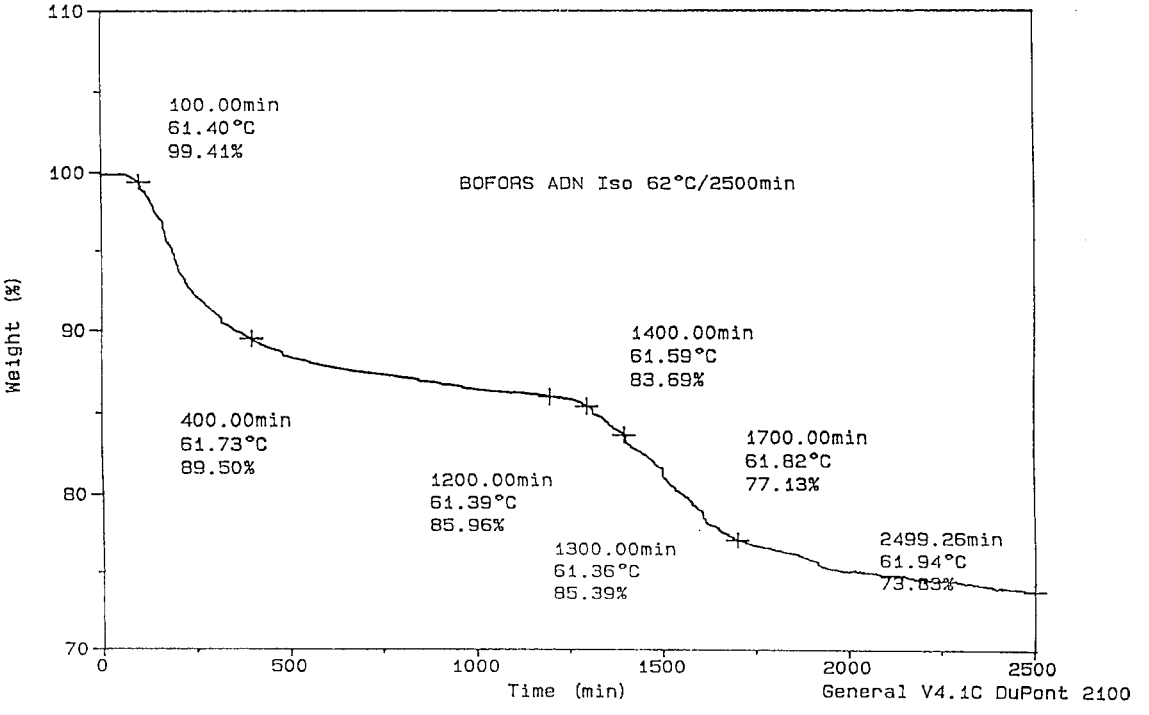

Fig. 14. Isothermal TG curve of BOFORS ADN in 35 mm vacuum at 62°C.

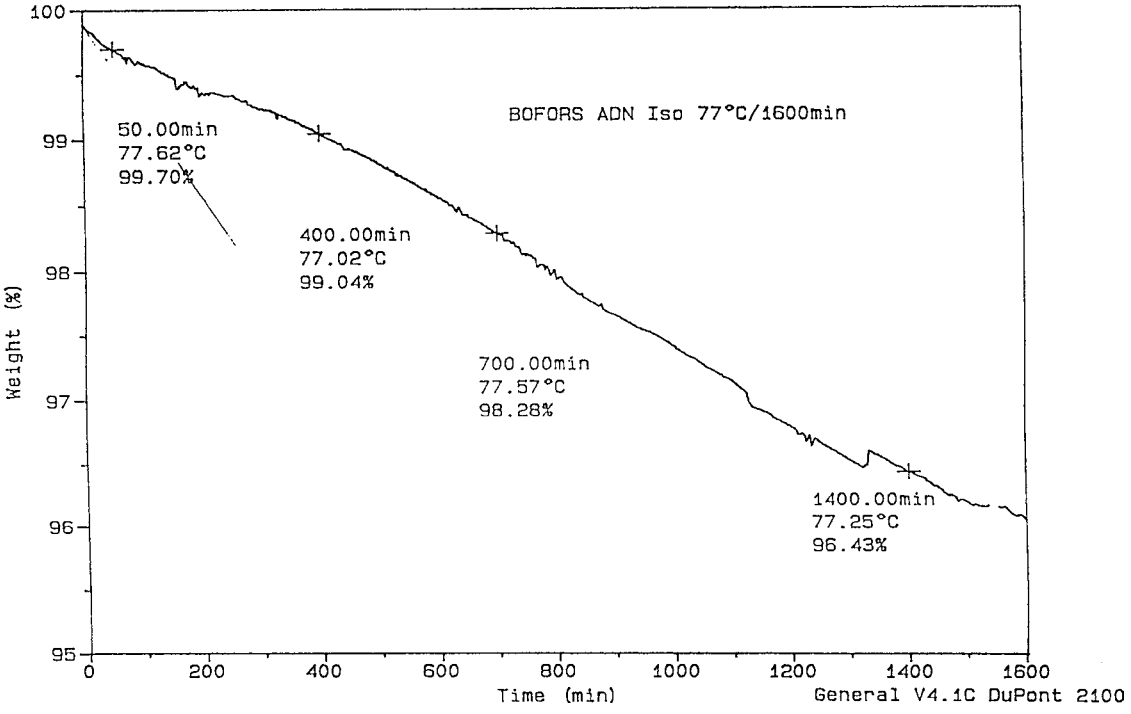

Fig. 15. Isothermal TG curve of BOFORS ADN in 35 mm vacuum at 77°C.

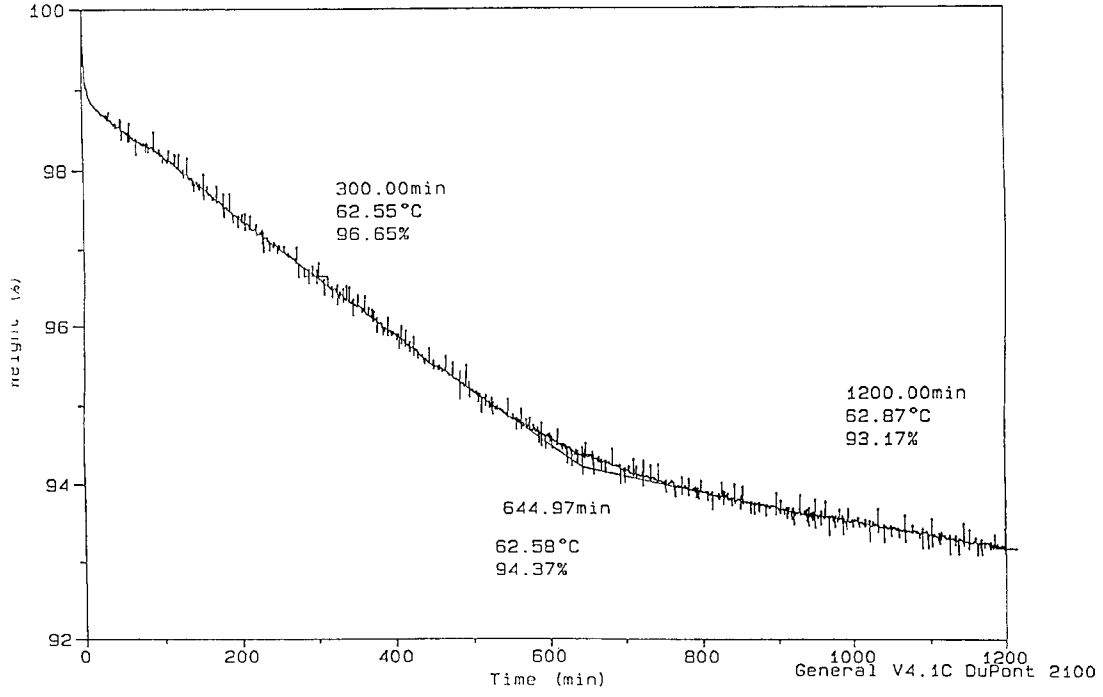

Fig. 16. Isothermal TG curve of NSWC ADN lot 50-4 in 35 mm vacuum at 62°C.

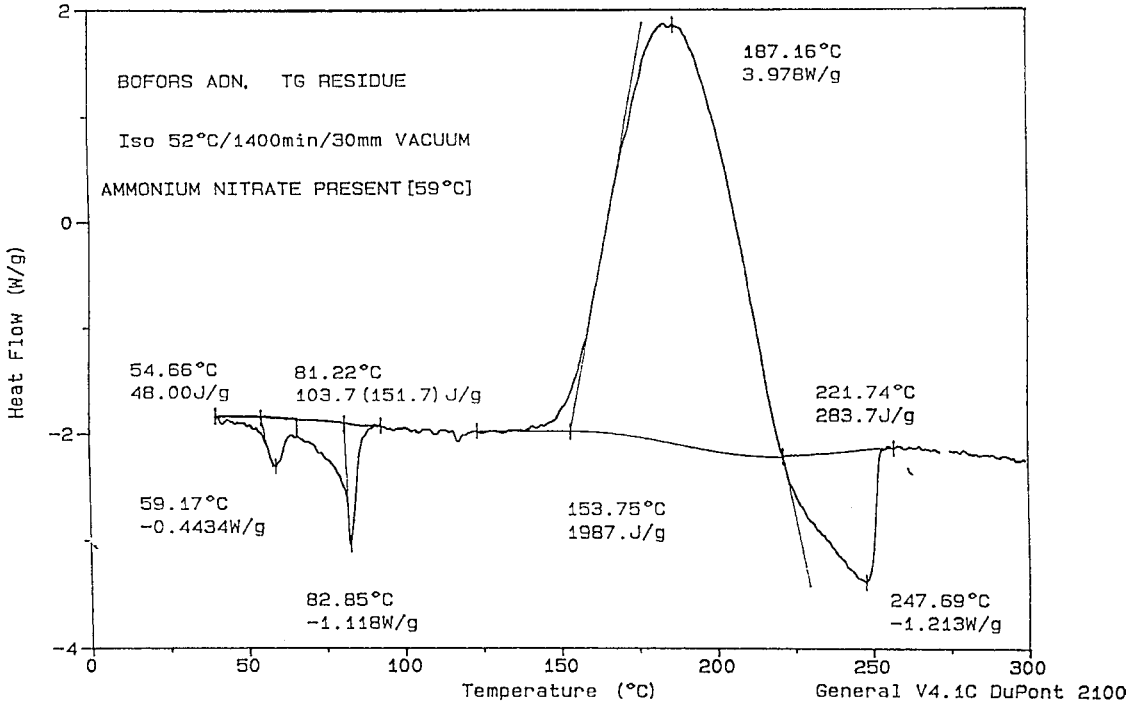

Fig. 17. DSC curve of BOFORS ADN TG residue (52°C) in nitrogen at 5°C/min.

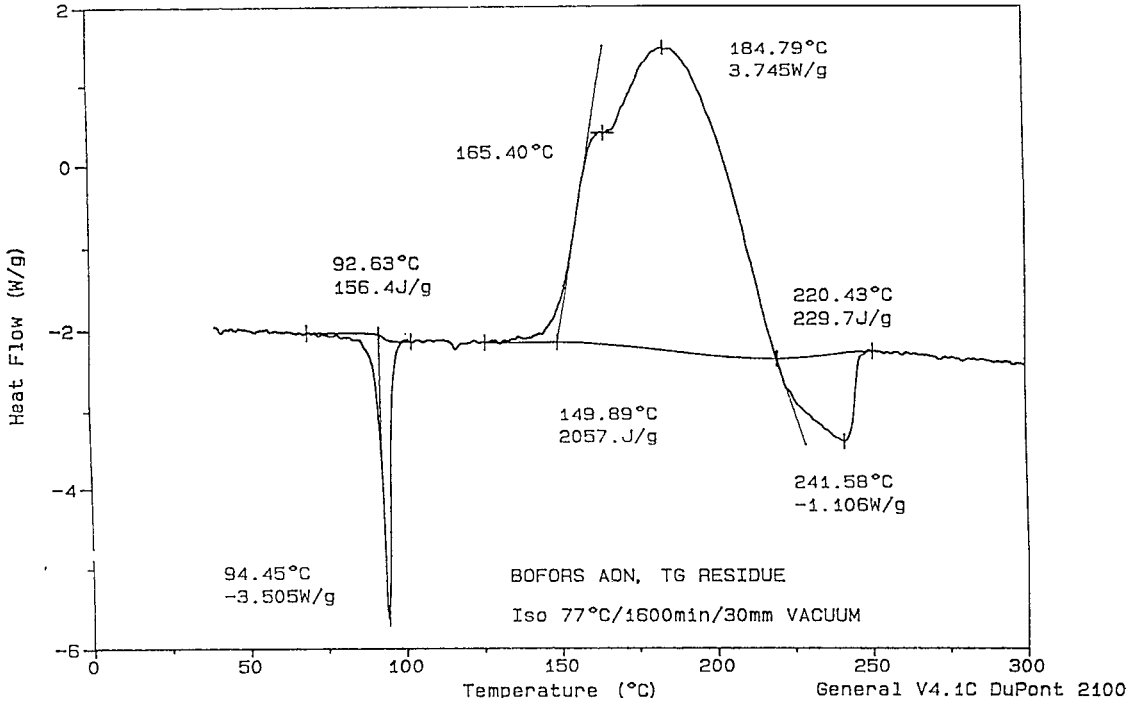

Fig. 18. DSC curve of BOFORS ADN TG residue (77°C) in nitrogen at 5°C/min.

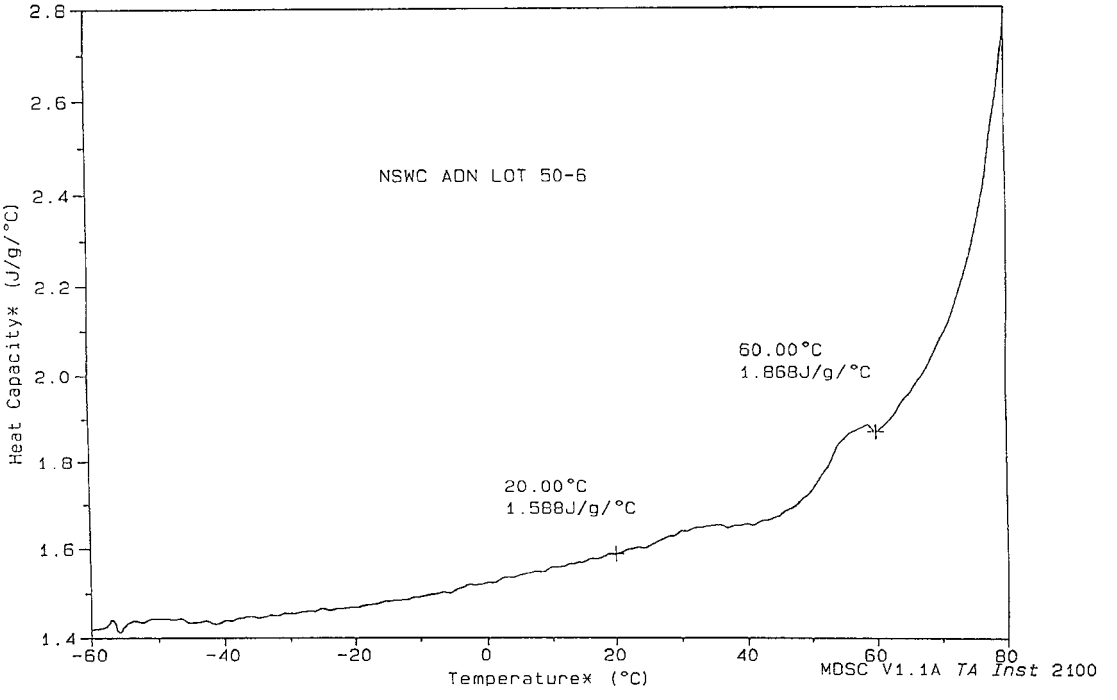

Fig. 19. MDSC heat capacity curve of NSWC ADN lot 50-6 in nitrogen at 1°C/min.

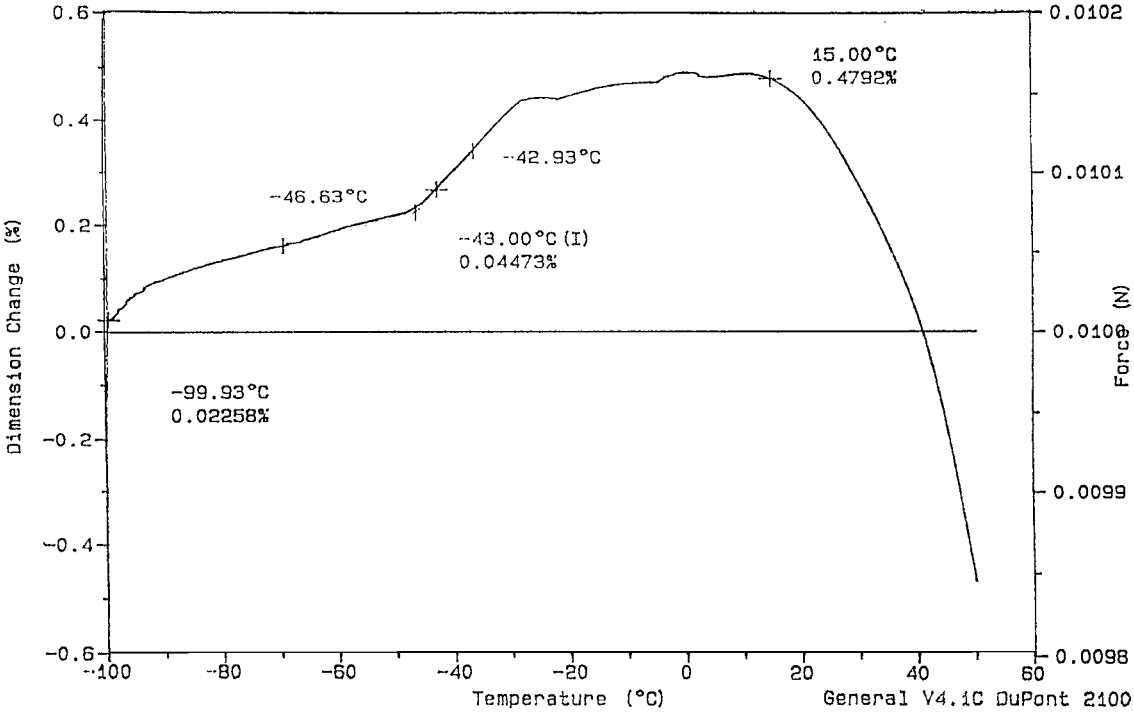

Fig. 20. TMA expansion curve of prilled ADN under a load of 0.01 N at 3°C/min.

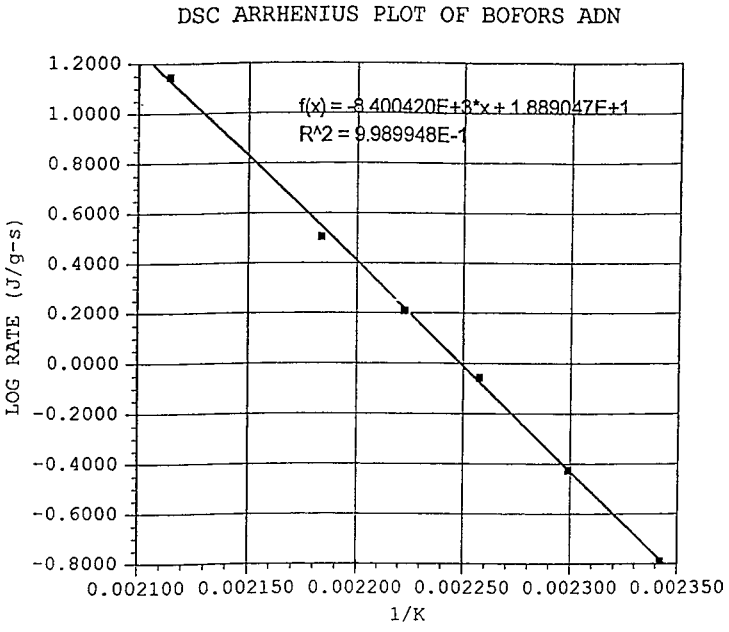

Fig. 21. DSC Arrhenius plot of BOFORS ADN in nitrogen.

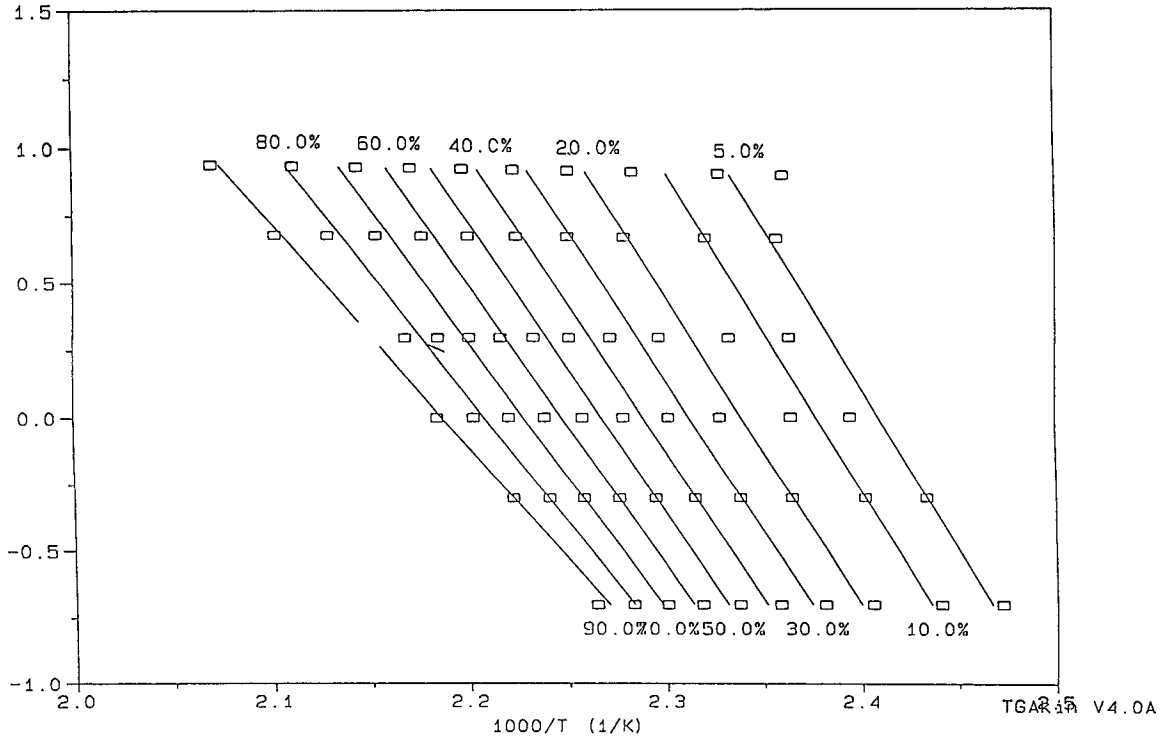

Fig. 22. TG Arrhenius plot of BOFORS ADN in nitrogen.

sample pans in nitrogen or helium had higher activation energies and frequency factors, namely 40–43 kcal/mol and 18–20 min^{-1}, respectively. Thus, it appears that confinement of the ADN decomposition gases either under pressurization or a sealed environment accelerates the decomposition of prilled ADN. Kinetics of decomposition of unprilled ADN at atmospheric pressure in nitrogen or helium by DSC and TG were E_a=37 kcal/mol and log A=17 min^{-1}. Unprilled ADN had lower activation energies and frequency factor for decomposition than prilled ADN which contained stabilizers. The effect of sample containment (i.e. aluminum, coated aluminum, gold, and glass ampoules) on the shape of the DSC curve of ADN was investigated. Isothermal TG in vacuum of ADN in the 45–75°C region and the DSC analysis of the TG residues showed unusual results in the 60°C region. The rate and enthalpy of decomposition of four dinitramide salts and their dielectric relaxation were related to the basicity of the cation.

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