

Thermal analysis of GAPTRIOL, an energetic azide polymer

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Abstract

GAPTRIOL is a non-linear glycidyl azide polymer used as the starting material to produce a binder in composite propellant formulations. The mechanism and energetics for the decomposition of GAPTRIOL are therefore of interest. Accordingly, this paper reports results of DSC, TGA and ARC measurements on GAPTRIOL. Discussion of these results and comparison with literature results for GAPDIOL, the linear analogue, are included. The decomposition of GAPDIOL has been reported as a first-order process. Results of kinetic studies on GAPTRIOL using both variable heating rate and isothermal techniques suggest that its decomposition is not a first-order process. In addition, TGA data show a two-stage weight loss in nitrogen and a four-stage weight loss in air. The kinetic information gleaned from the DSC and TGA measurements is compared with that extracted from the ARC data.

Keywords: ARC; Atmosphere; Azide; Decomposition; DSC; GAPTRIOL; Kinetics; Polymer; TGA

1. Introduction

Current activity in the development of rocket propellant formulations is directed towards producing formulations with low vulnerability and detectability. For this reason, much effort in this area has been devoted to the replacement, either partially or wholly, of the ammonium perchlorate (AP) in these formulations with other

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energetic oxidizers, such as ammonium nitrate (AN). Because AN is less energetic than AP, it is important to supplement such formulations with other energetic ingredients. An energetic binder frequently used for this purpose is GAP, glycidyl azide polymer.

Recently, there have been a number of publications in the scientific literature describing the properties of GAP [1–3]. The linear chain species, commonly called GAPDIOL, has two functional groups available for curing. The first step of the thermal decomposition of GAPDIOL is exothermic with an energy of -685 kJ mol^{-1} and is believed to be a result of conversion of the azide groups to cyano groups, thereby liberating nitrogen and hydrogen. An activation energy of 174 kJ mol^{-1} has been determined for this process from DTA measurements, and TGA measurements show a two-stage weight loss with 40% loss in the first stage between 410 and 550 K.

More recently, GAPTRIOL has been produced and used in propellant formulations. With a functionality approaching three, GAPTRIOL has the advantage of forming a more rigid binder network than that of GAPDIOL, when cured. Further, the enthalpy of formation of a multi-branched version of GAP is 176 kJ mol^{-1} , compared to only 119 kJ mol^{-1} for GAPDIOL [4]; hence more energy may be supplied from the combustion of GAPTRIOL. Because the thermal properties of GAPTRIOL have not been reported, the purpose of this paper is the presentation of results of extensive DSC, TGA and ARC measurements on this energetic polymer.

2. Experimental

GAPTRIOL was supplied by the Defence Research Establishment at Valcartier, Quebec via Rocketdyne Division, Rockwell International Corporation [5]. The material is a viscous, slightly yellow liquid of molar mass 2 kg mol^{-1} and was used without further treatment.

A TA 2100 Thermal Analyst with 910 DSC and 950 TGA modules was used with carrier gas flow of $50 \text{ cm}^3 \text{ min}^{-1}$. Dry oxygen-free nitrogen was used in both DSC and TGA measurements, and dry air was used in the TGA measurements.

The DSC was calibrated using indium and tin standards at each heating rate. Mercury was used as the standard for the low temperatures achieved with a Mechanical Cooling Accessory supplied by TA Instruments.

For the DSC measurements, 0.50 mg samples of GAPTRIOL were loaded into 5 mm^3 microampoules [6].

In the kinetic studies, heating rates from 2 to 10 K min^{-1} were used for both the DSC and TGA measurements [7, 8]. Samples were aged at 473 K for a period of 1 h, quenched, and subsequently subjected to a heating rate of 5 K min^{-1} for the purpose of determining the ΔH for decomposition of the remaining GAPTRIOL [7]. Isothermal DSC results at temperatures from 473 to 493 K were analyzed using the Isothermal Kinetics software produced by TA Instruments.

Pressure measurements in the DSC using a TA Pressure Cell were conducted in hermetic pans with pin holes.

A platinum sample boat was used for TGA measurements on 2 mg samples of GAPTRIOI. The microbalance of the TGA module was calibrated against a Mettler M3 electronic microbalance with reproducibility of $\pm 1 \mu\text{g}$.

2.1. ARC measurements

An accelerating rate calorimeter (ARC) was used to test the thermal stability of 0.25 g samples of GAPTRIOI. The ARC was developed by Dow Chemical Company and has been licensed to Columbia Scientific Industries of Austin, Texas. It has been used to estimate the hazard potential of energetic materials.

The ARC is an automated instrument from which experimental results may be determined for an exothermic process occurring in an adiabatic environment. A description of the thermokinetic information available from the ARC has been published previously [9].

To operate the ARC, equilibration at a starting temperature is followed by an iterative “heat-wait-search” technique until the appearance of a self-heating rate above a preset threshold limit. The temperature T_i at which this occurs is referred to as the onset temperature. When an exotherm is detected, time, temperature, rate of temperature increase and pressure are monitored continuously until the condition of the preset limit is no longer met. At this point, the exothermic process is considered complete and the temperature at which this occurs is T_f .

3. Results and discussion

3.1. DSC results

The DSC thermogram and TGA results for GAPTRIOI at 10 K min^{-1} are compared in Fig. 1. A single exotherm with an onset temperature of $501 \pm 1 \text{ K}$ and ΔH of $2.58 \pm 0.05 \text{ kJ g}^{-1}$ was observed. The onset temperature was obtained from

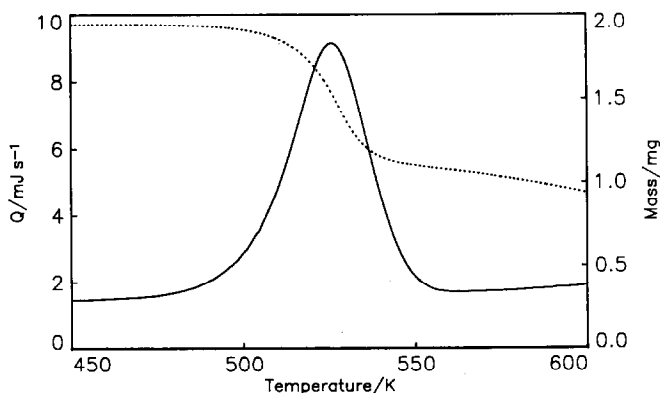


Fig. 1. DSC and TGA (in nitrogen) of GAPTRIOI at $\beta = 10 \text{ K min}^{-1}$.

the point of intersection of the tangent, drawn at the point of maximum slope of the leading edge, and the extrapolated base line. The exotherm corresponds with the initial weight loss observed in the TGA experiments done in nitrogen.

The variable heating rate results were analyzed by plotting $\ln(\beta/T^2)$ against $1/T$ [7], where β is the heating rate and T is the peak temperature, corrected for thermal lag. It is assumed that the Arrhenius equation

$$k = Ze^{-E/RT} \quad (1)$$

adequately expresses the temperature dependence of the reaction rate constant k ; the results for the pre-exponential factor Z and the activation energy E determined from the above analysis are given in Table 1.

Aging tests gave results for the fraction of unreacted GAPTRIOI, α , which agreed with that predicted from the kinetic parameters, Z and E in Table 1, within $\pm 6\%$.

The results for the isothermal DSC experiments were analyzed in terms of the model

$$-\frac{d\alpha}{dt} = kg(\alpha) \quad (2)$$

where $d\alpha/dt$ is the reaction rate and

$$g(\alpha) = \alpha^n \quad (3)$$

The results for Z , E and n for this model are listed in Table 1.

The order n was found to decrease from $n = 1$ to $n = 0.8$ with increasing temperature. The reaction is first order at low temperatures where low conversion occurs. At higher temperatures, higher conversion results in increased pressure and a consequent decrease in the reaction rate. The apparent order of the reaction is thus decreased. It is estimated that the pressure increases to approximately 80 bar when complete conversion takes place.

The pressure coefficient of ΔH for the decomposition of GAPTRIOI was estimated as $6.0 \pm 1.0 \text{ J g}^{-1} \text{ bar}^{-1}$, from measurements at nominal pressures of 14 bar (200 p.s.i.) and 55 bar (800 p.s.i.). A slight decrease in the onset and peak temperatures with increasing pressure was observed. More significantly, at 55 bar,

Table 1
Kinetic parameters for GAPTRIOI determined by various thermoanalytical techniques^a

Parameters	DSC ^b	DSC ^c	TGA	ARC
$E/\text{kJ mol}^{-1}$	160 ± 5	178 ± 5	155 ± 10	182 ± 2
$\ln(Z/\text{min}^{-1})$	25.04 ± 0.05	41.0 ± 1.2	34.92 ± 0.08	42.15 ± 0.06
n	1	0.78 ± 0.04	1	0.88 ± 0.02

^a The uncertainties are standard deviations calculated from the point scatter in a single determination for the DSC^b and ARC measurements and from multiple determination of the kinetic constants for the other measurements. ^b Variable heating rate method. ^c Isothermal method.

an additional exotherm appeared at 426 K with a ΔH of 0.12 ± 0.05 kJ g⁻¹. Thus, it appears that a competing decomposition process of lower activation energy is available at high pressures.

Finally, the glass transition temperature T_g was found to be 225.8 ± 0.3 K. T_g was determined by cooling a 5.0 mg sample in a hermetic pan to 190 K, equilibrating at that temperature and heating at 5 K min⁻¹ through the glass transition. The value for the T_g of GAPDIOL has been reported as 225 K [4].

3.2. TGA results

The results for GAPTRIOL in nitrogen are shown in Fig. 1. The total weight loss is 55% with a 36% loss in the first stage. The first-stage weight loss may be compared with that of 31% predicted assuming that the glycidyl azide repeating unit is converted to the cyano analogue, nitrogen and hydrogen. This apparent first-order reaction is relatively rapid compared with the second-stage reaction.

The peak temperatures obtained from the derivative curves in the variable heating rate study in the TGA are compared with those from the corresponding DSC measurements in Table 2. Peak temperatures for the TGA measurements are generally higher due to differences in experimental conditions, notably larger sample size and the use of an open system.

Figure 2 illustrates the analysis of the variable heating rate results at constant conversion, for the purpose of determining the kinetic parameters [8]. Similar analysis for weight losses between 4% and 14% resulted in the Z and E values shown in Table 1.

Use of larger sample sizes and/or higher heating rates frequently resulted in violent reactions; for example, a 12 mg sample heated at 2 K min⁻¹ “exploded” at 504 K.

In Fig. 3, the TGA results for GAPTRIOL in nitrogen and air are compared. In air, there are four stages of weight loss, with the intermediate stages apparently corresponding to those seen for the experiments done in nitrogen. The last stage is a result of complete oxidation of the remaining polymer chain; however, the oxidation process occurring in the first stage is not known.

Table 2
Comparison of peak temperatures in K determined by DSC and TGA measurements

β /K min ⁻¹	DSC	TGA ^a
2	504.4	507.7
4	514.0	514.9
6	518.7	521.1
8	523.3	523.5
10	525.7	527.3

^a From derivative curve.

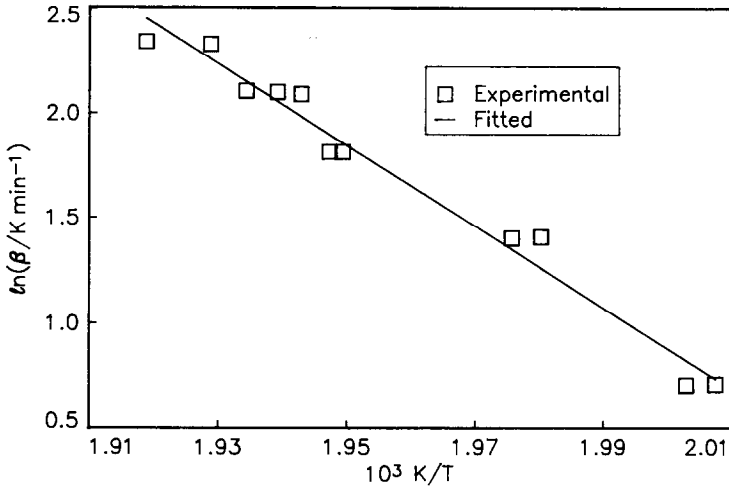


Fig. 2. Fit of $\ln(\beta/K \text{ min}^{-1})$ for 10.0% mass loss in TGA experiments on GAPTRIOI.

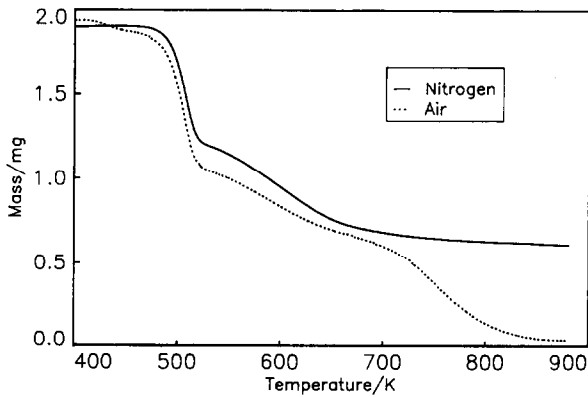


Fig. 3. TGA of GAPTRIOI at $\beta = 2 \text{ K min}^{-1}$ in nitrogen and air.

3.3. ARC results

The ARC results for GAPTRIOI are shown in Fig. 4. Onset occurs at $T_i = 442 \pm 3 \text{ K}$ and the parameters at maximum rate are $T = 474 \pm 3 \text{ K}$, $p = 6.5 \pm 0.2 \text{ bar}$ and $t = 6.7 \pm 1.2 \text{ h}$. The lower onset temperature observed in the ARC experiments is a direct result of the larger sample size relative to that used in the DSC experiments.

The data from the ARC measurements have been used to estimate kinetic parameters. The fraction of unreacted GAPTRIOI $\alpha(t)$ is assumed to be related to the difference between T_f and the temperature $T(t)$ by

$$\alpha(t) = (T_f - T(t))/\Delta T \quad (4)$$

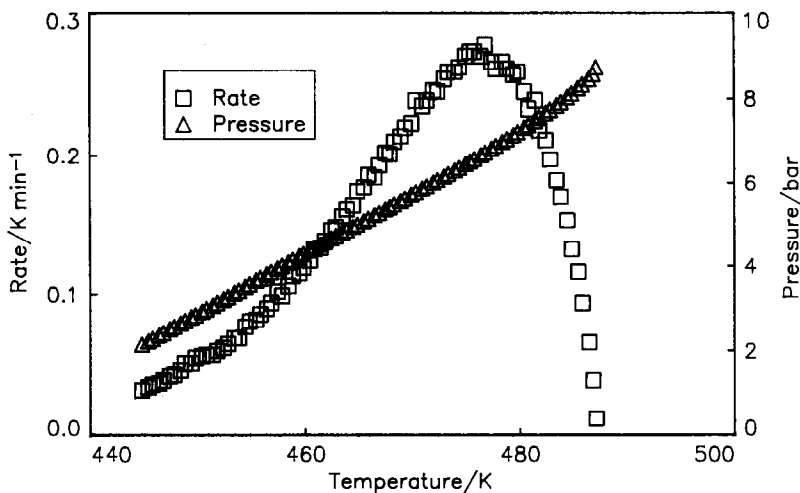
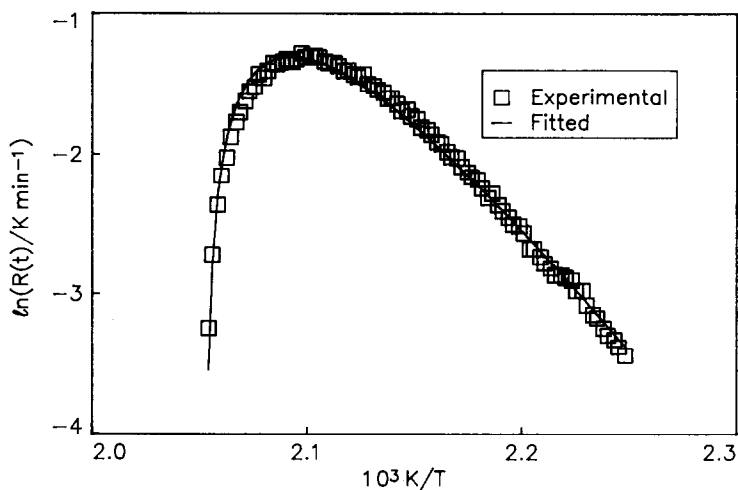


Fig. 4. Rate and pressure data from ARC experiments on GAPTRIOIOL.

Fig. 5. Fit of $\ln(R(t)/K \text{ min}^{-1})$ according to Eq. (6).

where $\Delta T = T_f - T_i$. The self-heating rate, $R(t) = dT(t)/dt$, can be expressed in terms of $d\alpha/dt$ as follows

$$\frac{d\alpha}{dt} = R(t) \frac{d\alpha}{dT} \quad (5)$$

From Eqs. (1) and (3)–(5), it can be shown that

$$\ln[R(t)] = n \ln[T_f - T(t)] - E/RT(t) + A \quad (6)$$

where A is a constant defined by $A = \ln[Z/\Delta T^{n-1}]$.

The results obtained by fitting the experimental data for $R(t)$ to the independent variables in Eq. (6) are illustrated in Fig. 5. Values for n , E and Z are recorded in Table 1 where they are compared with results from the DSC and TGA experiments. It is noted that there is reasonable agreement, particularly between the parameters determined from the ARC measurements and those determined from the isothermal DSC experiments.

4. Conclusions

Both the ARC results and those from isothermal kinetics studies in the DSC indicate that the decomposition of GAPTRIOIOL is not a simple first-order process. This observation may be a direct result of the increase in pressure as decomposition proceeds in a closed system. The appearance of a second exotherm at higher pressure supports this conclusion. In contrast, a relatively rapid and known first stage is followed by a relatively slow second stage of unknown origin, in open or dynamic systems.

5. References

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