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THERMAL ANALYSIS STUDIES ON ISOPROPYLNITRATE

D. E. G. Jones, H. T. Feng, R. A. Augsten and R. C. Fouchard

Canadian Explosives Research Laboratory, 555 Booth Street, Ottawa, ON K1A 0G1, Canada

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Abstract

Isopropylnitrate (IPN) is described as a detonable material used in propellants and explosives. While there is considerable information available on its sensitivity and compatibility with other materials, very little is known about its thermochemical properties. This paper will describe the results obtained from some DSC, heat flux calorimetry (HFC) and accelerating rate calorimetry (ARC) measurements.

The ASTM DSC method using a hermetic aluminum pan having a lid with a laser-produced pin hole was used to determine the vapour pressure of $IPN_{(l)}$. Results calculated from an Antoine equation are in substantial agreement with those determined from DSC measurements. From the latter measurements, the enthalpy of vaporization was determined to be 35.32±0.62 kJ mol^{-1}. Attempts to determine vapour pressures above about 0.8 MPa resulted in significant decomposition of $IPN_{(g)}$.

The enthalpy change for decomposition in sealed glass systems was found to be –3.43± 0.09 kJ g^{-1} and –3.85±0.03 kJ g^{-1}, respectively from DSC and HFC measurements on $IPN_{(l)}$ samples loaded in air. Slightly larger exotherms were observed for the HFC results in air than those in inert gas, suggesting some oxidation occurs. In contrast, no significant difference in the observed onset temperature of about 150°C was observed for both the HFC and ARC results.

From DSC measurements, an Arrhenius activation energy for decomposition of 126± 4 kJ mol^{-1} was found. These measurements were also conducted in sealed glass systems and decomposition appeared to proceed primarily from the liquid phase.

Keywords: ARC, DSC, HFC, kinetics

Introduction

The thermal properties and derived information for energetic materials, such as propellants, are currently the subject of considerable interest. Isopropylnitrate (IPN) is a monergolic propellant, for which early results of limited vapour pressure, mechanical sensitivity and compatibility measurements have been compiled [1]. Recently, a number of thermal [2, 3], ignition [4] and pyrolysis [5] studies have been reported for the gas phase decomposition of IPN. Hiskey *et al.* [6] have studied the rates of thermal decomposition of IPN in tetralin solvent at

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temperatures from 155 to 195°C. They found an activation energy of 191 kJ mol^{-1} and concluded that the isopropyl group (radical stabilizing) favours beta scission. Further, an activation energy of 170 kJ mol^{-1} [7] has been obtained for the thermal decomposition of $IPN_{(g)}$, from measurements in a single pulse shock tube. This paper reports a detailed investigation of the vapour pressure from ambient to 200°C and a comparative study of the decomposition of IPN using a variety of thermal techniques.

Experimental

Chemical

IPN of purity 99 mol% was obtained from Aldrich Chemical Company and was used without further purification.

Differential scanning calorimetry (DSC)

For the vapour pressure measurements, in accordance with ASTM E 1782 [8], a TA 2100 Thermal Analysis System with a 2910 DSC module was used with a carrier gas flow of 50 cm^3 min^{-1}. The carrier gas was dry oxygen-free nitrogen, a heating rate of 5°C min^{-1} was used and an aluminum hermetic pan with a laser pin-hole vented lid contained IPN samples (about 5 mg) and calibration standards in the DSC measurements. In some cases, a teflon-coated hermetic aluminum pan was used for the experiments.

The DSC was calibrated for heat flow and temperature using SRM biphenyl and traceable indium standards. The calibration was verified and only the value of the heat of fusion of indium within 3% of the literature value was accepted. Calibration was carried out at the pressure used, although ASTM E 1782 does not require this, since the pressure effect is claimed to be small. The apparatus and details of the procedure are described in [9]. The method was verified using a sample of distilled, deionized water with a conductivity less than $1\cdot10^{-5}$ S m^{-1}, at various pressures.

In the kinetic studies, the above system was also used except that heating rates from 2–10°C min^{-1} were employed, following the procedure of ASTM E 698 [10]. At each heating rate, the DSC was calibrated for heat flow using the SRM standards biphenyl, indium (traceable), tin, lead and zinc.

For the kinetic measurements, standards and samples of about 1 mg $IPN_{(l)}$ were sealed in glass microampoules. A silver tray with a diameter of about 8 mm was wrapped around the microampoule and flattened on the side in contact with the sample platform in the DSC. More details about this technique are provided in [11] and [12].

Heat flux calorimetry (HFC)

The manifold and special high pressure vessels for the HFC measurements, conducted in both Ar and air environments, are described in [13].The following two methods were used for loading samples: (i) the samples were loaded directly into the high pressure vessel and the pressure change was recorded during the experiment or, alternatively, a pressure was applied prior to starting the experiment and (ii) the samples were sealed in a glass ampoule which had an internal volume of about 0.7 cm^3. The glass ampoule was loaded in the high pressure vessel and a helium environment was used to provide good thermal conductivity between the ampoule and the vessel. For both methods, sample size was less than about 50 mg and a heating rate of 0.3°C min^{-1} was used.

Accelerating rate calorimetry (ARC)

The instrument used for ARC measurements is a commercial automated adiabatic calorimeter distributed by Arthur D. Little Inc. and used for the purpose of assessing the thermal hazard potential of energetic materials [14]. Adiabatic conditions are maintained in this instrument provided that the rate of temperature rise does not exceed about 10°C min^{-1}. Samples of about 0.5 g of $IPN_{(l)}$ were placed in lightweight spherical titanium vessels, which were closed in order to maintain any pressure resulting from vaporization or decomposition of the sample. Experiments were carried out in both Ar and in air. The standard ARC procedure of 'heat-wait-search' was used; the temperature of the system was raised by 5°C, the system was maintained adiabatic both during periods of dissipation of thermal transients and of 'search' for an exotherm defined as a self-heating rate exceeding 0.02°C min^{-1}.

Results

Vapour pressure

Vapour pressures for $IPN_{(l)}$ were determined from DSC measurements following the ASTM procedure [8] and using our specific method and apparatus [9]. Sample results for pressures from subambient to superambient are depicted in Fig. 1. These results were obtained in spite of the considerable experimental difficulty experienced with mass loss of IPN after sealing the sample in the hermetic pan. Some experiments were repeated using teflon-coated Al pans in order to confirm chemical compatibility between Al and $IPN_{(l)}$. Smooth DSC curves were obtained for all pressures ranging from about 3 kPa up to about 0.4 MPa, allowing precise determination of the extrapolated onset temperature. Significant decomposition of $IPN_{(g)}$ occurs beyond 0.4 MPa and this prevents precise determination of the baseline at the end of the endotherm. Figure 1 shows this decomposition occurring as a doublet at about 0.8 MPa.

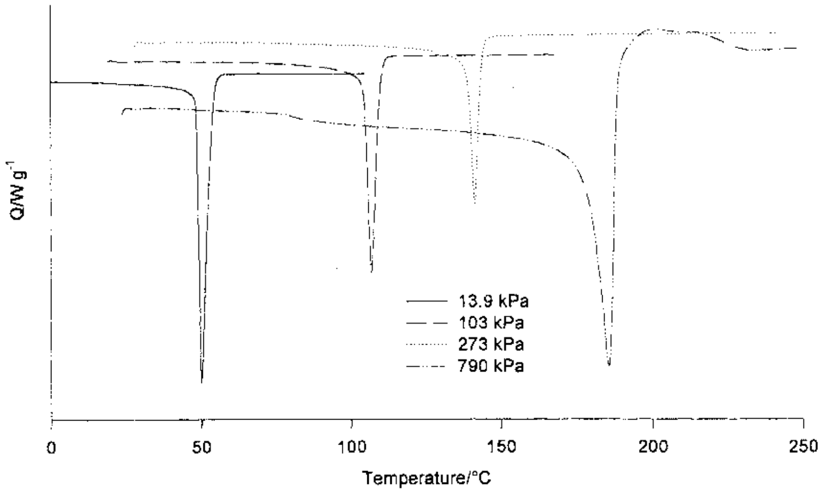

Fig. 1 Vapour pressure results for IPN from DSC measurements

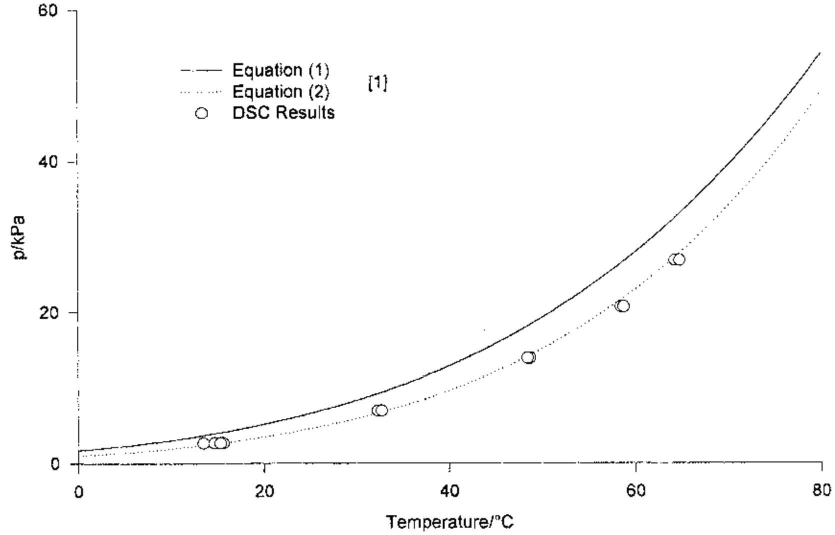

Fig. 2 Comparison of vapour pressure data for IPN with literature data

Our vapour pressure data are compared with literature results [1] in Fig. 2. It is noted that the literature results are very old and apparently valid only for pressures below about 25 kPa. While this reference cites two equations for calculating vapour pressures, results of actual measurements are only provided below 2 kPa. From Fig. 2, it can be seen that our subambient pressure data agree remarkably well with Eq. (2) (an Antoine equation).

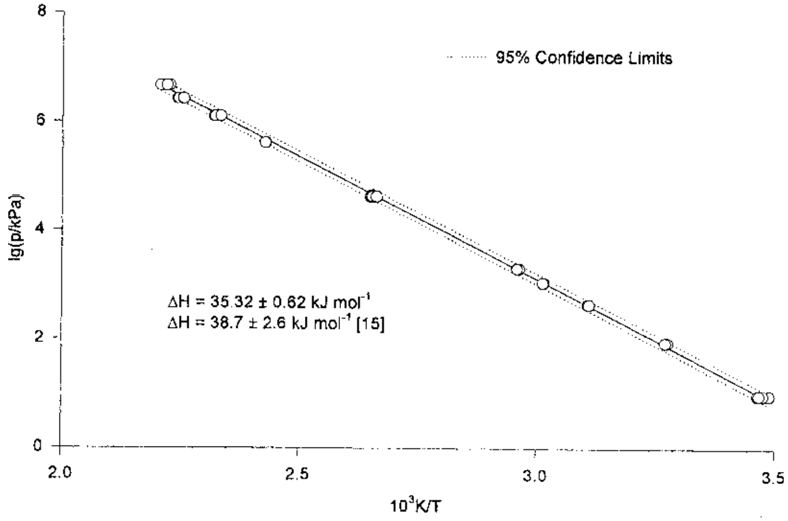

Fig. 3 Clausius-Clapeyron plot of DSC vapour pressure data

In Fig. 3, the Clausius-Clapeyron plot of all the DSC data is shown and from this plot ΔH_{vap}=35.32±0.62 kJ mol^{-1}. This result compares favourably with the value of ΔH_{vap}=38.7±2.6 kJ mol^{-1}, estimated from $\Delta_f H$ (IPN$_{(l)}$) and $\Delta_f H$ (IPN$_{(g)}$) [15].

Decomposition studies

DSC

Figure 4 shows a sample DSC curve for the decomposition of IPN$_{(l)}$ in a sealed glass microampoule at β=10°C min^{-1}. Observation under a microscope of an IPN$_{(l)}$ sample as it is heated over 200°C suggests that decomposition takes place primarily in the liquid phase, in this closed system. Accordingly, the variable heating rate study employed in the ASTM method [10] is believed to provide kinetic parameters for the liquid phase decomposition. The results for this study are given in Fig. 5, from which the activation energy, E_a=126±4 kJ mol^{-1} and lg(Z/min^{-1})=30.06±0.07, where Z is the pre-exponential factor in the Arrhenius equation. The scatter in the data in Fig. 5 reflects the difficulty in sealing the microampoules as a result of the volatility of IPN$_{(l)}$. This difficulty is also apparent from the considerable variation in the ΔH values throughout the variable heating rate study. However, five trials at β=10°C min^{-1} did produce a consistent value, namely ΔH=–3.43±0.09 kJ g^{-1}. Finally, successive trials of the half-life test [10] yielded results in excellent agreement with one another but somewhat lower than expected based on the value of ΔH above.

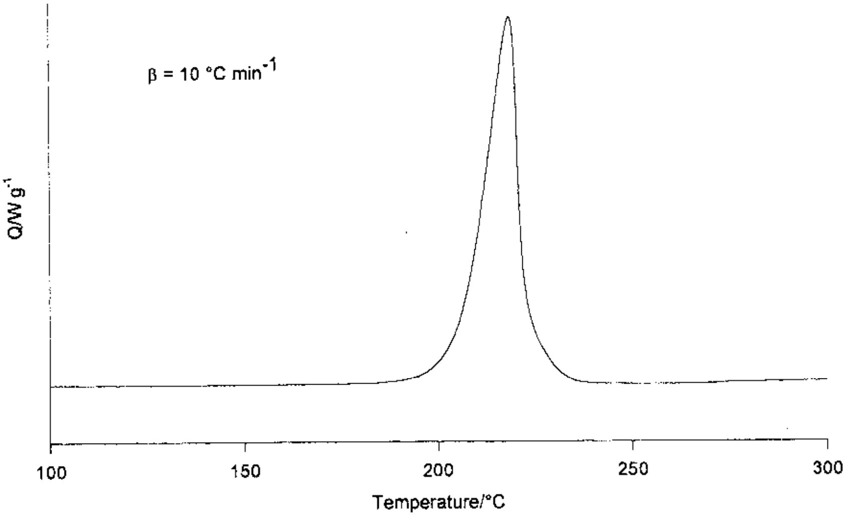

Fig. 4 DSC result for IPN sample sealed in glass microampoule

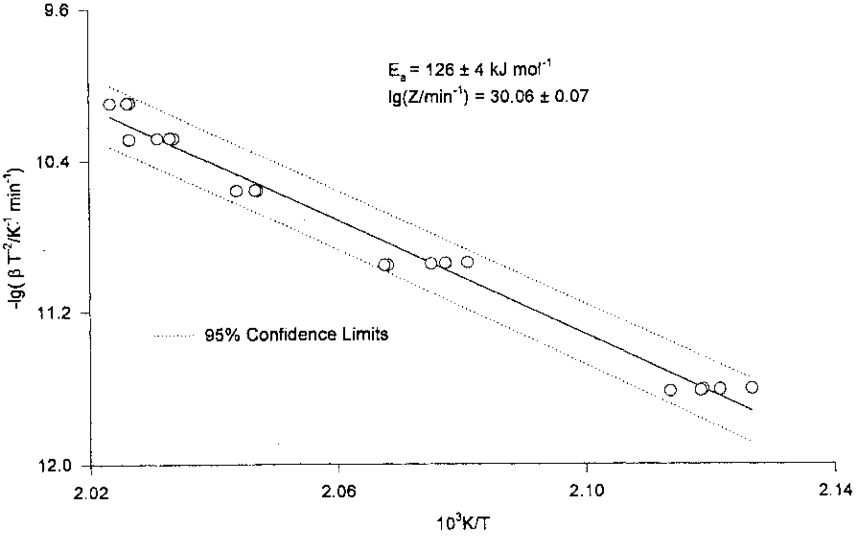

Fig. 5 Kinetic results obtained using ASTM E698

HFC

HFC curves for 50 mg samples of $IPN_{(l)}$ in ampoules loaded in an Ar and in an air environment are compared in Fig. 6. At 0.02°C min^{-1}, the onset temperature decreases significantly, to about 130°C. The results at 0.3°C min^{-1} give

ΔH(Ar)=–3.65±0.13 kJ g^{-1} and ΔH(air)=–3.85±0.03 kJ g^{-1}. The latter result is in satisfactory agreement with the predicted value, ΔH=–4.2 kJ g^{-1} for the reaction:

$$2\mathrm{IPN}_{(l)} + 0.5\mathrm{O}_{2(g)} = 4\mathrm{CO}_{(g)} + 2\mathrm{CH}_{4(g)} + \mathrm{N}_{2(g)} + 3\mathrm{H}_2\mathrm{O}_{(g)}$$

These curves yield an onset temperature of 150±2°C for the decomposition of $\mathrm{IPN}_{(l)}$, independent of the gas environment.

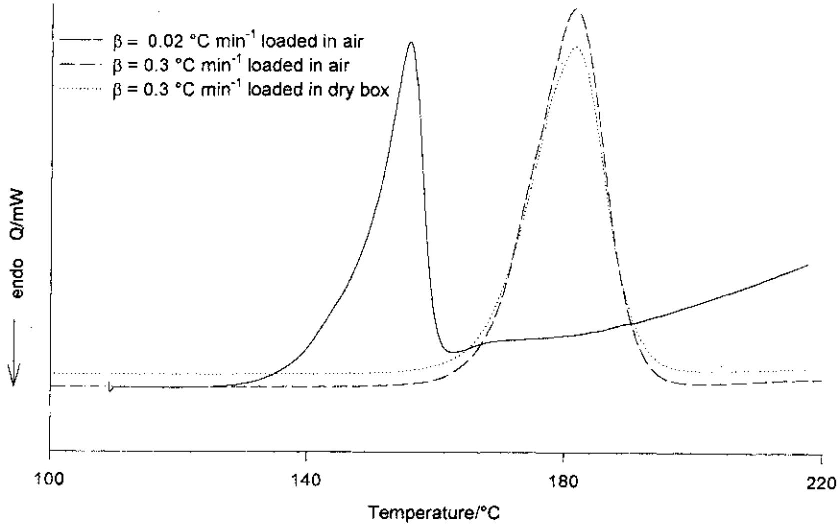

Fig. 6 HFC results for IPN in glass ampoule loaded in air and in argon

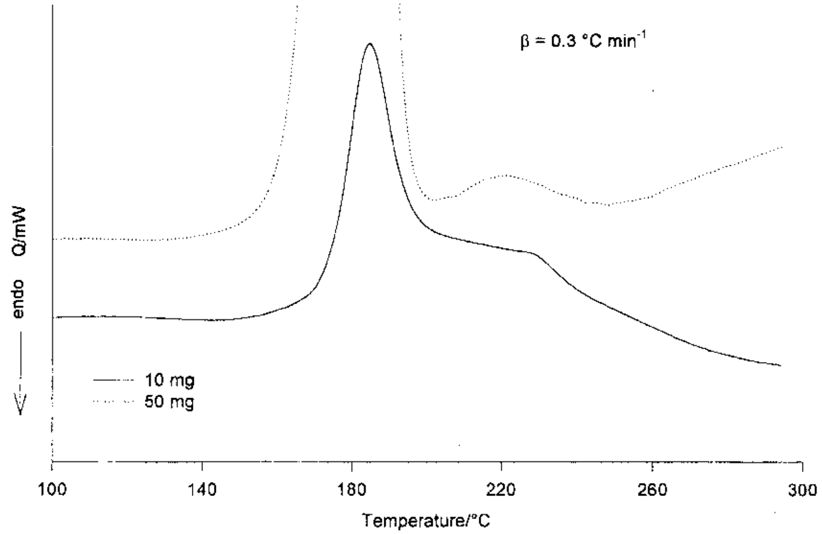

Fig. 7 HFC results for IPN of different sample sizes loaded in air

In Fig. 7, HFC curves are shown for 11 and 50 mg samples of $IPN_{(l)}$ sealed in ampoules in air. For the 11 mg sample, significantly more of the secondary reaction occurs and this reaction appears to be the result of either enhanced oxidation or additional $IPN_{(g)}$ decomposition because of the added free volume in the ampoule.

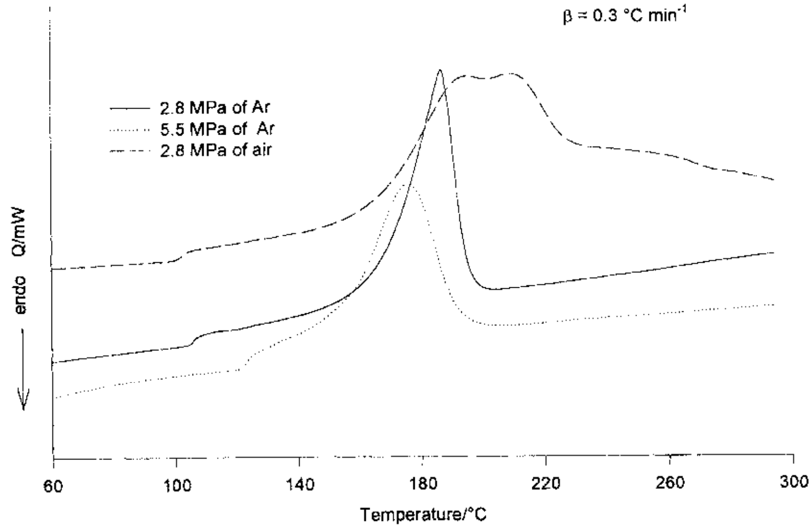

Fig. 8 HFC results for IPN in both air and argon under pressure

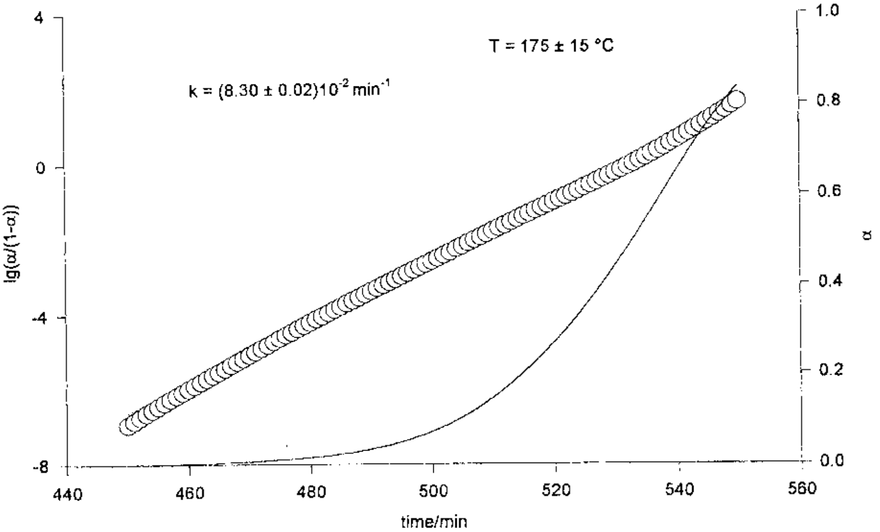

Fig. 9 Fit of decomposition results to Prout-Tompkins equation

Figure 8 compares HFC results for IPN in air and Ar at p=2.8 MPa and also results in Ar at p=5.5 MPa. It is clear that the decomposition in air is complex, resulting in a doublet peak, followed by a significant later reaction which appears to be incomplete at the end of the experiment. In contrast, the decomposition in Ar results in a single sharp peak with a ΔH=–4.0 kJ g^{-1}. It is noted that $\Delta T/\Delta P$=–2.1 K MPa^{-1}, suggesting increased reactivity of IPN$_{(l)}$ at higher pressure. The discontinuity prior to the exotherm observed in all curves is believed to be the critical point for IPN, the temperature of which is, as expected, dependent on the starting pressure.

Finally, Fig. 9 shows the results obtained by fitting the data from Fig. 7 (air) to the Prout-Tompkins equation. The fit is satisfactory in spite of the fact there is a small temperature change during the period of the reaction analyzed and also that this equation is normally applied to solid phase decomposition processes.

ARC

ARC results for IPN$_{(l)}$ in Ar and air are in substantial agreement with one another and these results are illustrated in Figs 10 and 11. The 'true' onset temperature is 145±10°C for 0.5 g IPN$_{(l)}$ but no experimental studies were conducted to determine any possible dependence of this temperature on mass. There is no discernable difference between the results in air and in Ar for the post-run residual mass and pressure at ambient conditions.

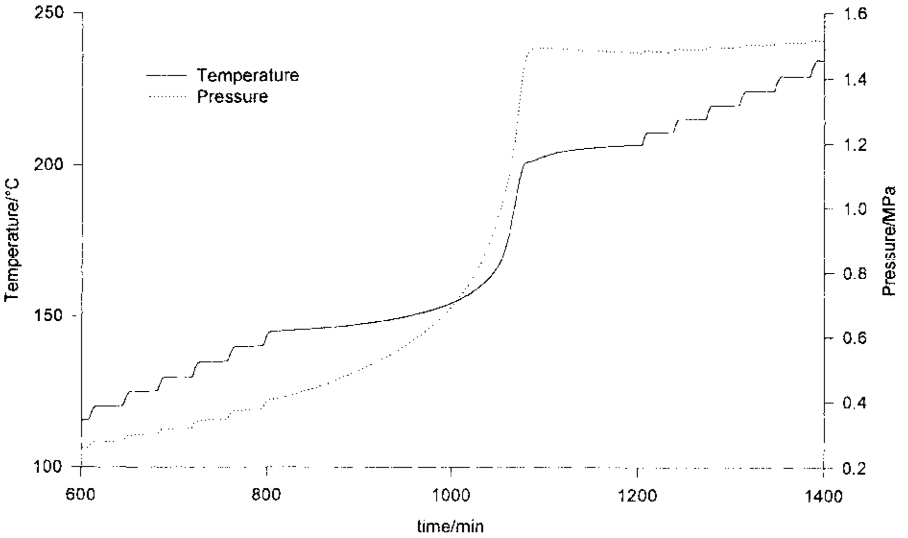

Fig. 10 ARC results for IPN in Ar

Figure 12 depicts the results obtained when the rate data are analyzed as described in [16],using the equation

$$\lg[R(t)] = n\lg[T_f - T(t)] - \frac{E_a}{RT(t)} + A$$

where $A=\lg[Z/\Delta T^{n-1}]$, n is the reaction order, T_f and T_i are respectively the final and initial temperatures when $R(t)\geq 0.02$°C min^{-1} and $\Delta T=T_f-T_i$. This analysis yields $E_a=229\pm5$ kJ mol^{-1}, $\lg(Z/\text{min}^{-1})=58.5\pm0.3$ and $n=2.14\pm0.05$. Similarly

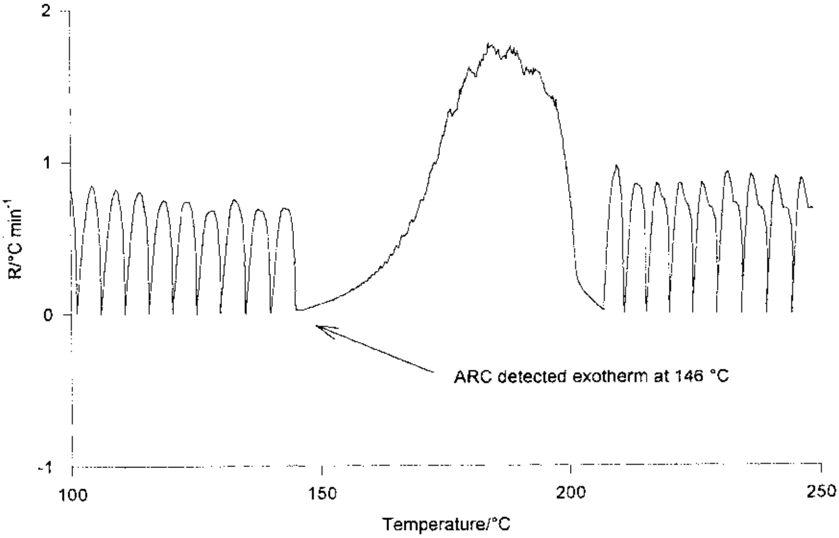

Fig. 11 Self-heating rate for IPN in Ar

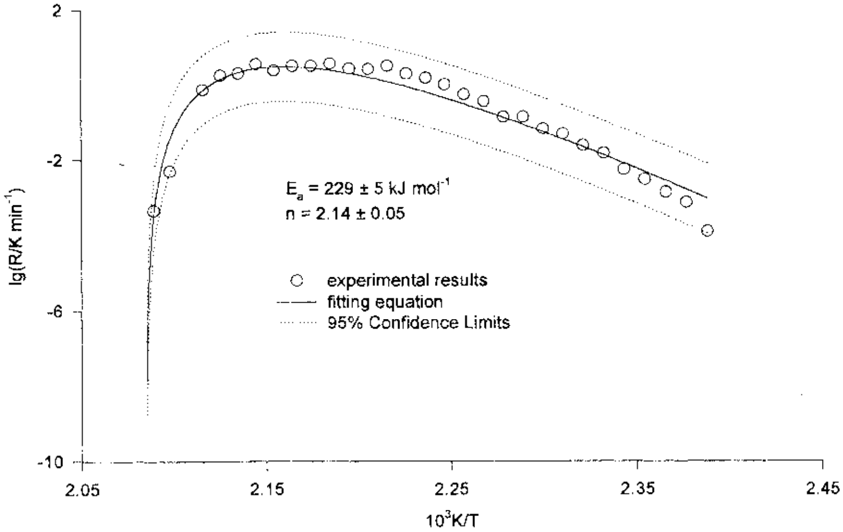

Fig. 12 Analysis of ARC results

analysis of the data for the initial period of the decomposition, for which the plot in Fig. 12 is linear gives E_a=178±5 kJ mol^{-1}. The generally larger value of E_a compared with that obtained from the DSC data indicates that a significant amount of IPN$_{(g)}$ decomposition occurs in the ARC studies.

Conclusions

The ASTM technique gives reliable results for the vapour pressure of IPN$_{(l)}$ up to the temperature at which IPN$_{(g)}$ decomposes, yielding a precise value of the enthalpy of vaporization. In decomposition studies, the activation energy obtained from DSC measurements is significantly lower than that reported in the literature for IPN$_{(g)}$ and also that obtained from ARC results, suggesting that decomposition is predominantly from the liquid phase given the experimental conditions used in the DSC. Decomposition energetics of about –4 kJ mol^{-1} are obtained from both the DSC and HFC measurements, the latter slightly more exothermic in air. An onset temperature of about 150°C was obtained from both the ARC and HFC results.

Using high initial pressures produced single, sharp peaks for decomposition in Ar with comparable energy values to that observed starting at ambient pressure, in contrast with the results in air, which show complex behaviour as a result of oxidation. In both cases, a sharply defined critical point, which is dependent on the initial pressure, was observed.

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