Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Thermochimica Acta 401 (2003) 17–25

thermochimica acta

www.elsevier.com/locate/tca

Combined use of adiabatic calorimetry and heat conduction calorimetry for quantifying propellant cook-off hazards☆

P.F. Bunyan[a,*], T.T. Griffiths[a], V.J. Norris[b]

[a] *QinetiQ, Centre for Environmental Technology, Building X48, Fort Halstead, Sevenoaks, Kent TN14 7BP, UK*
[b] *QinetiQ, Centre for Environmental Technology, Bishopton, Scotland PA7 5NJ, UK*

Received 12 June 2002; received in revised form 30 September 2002; accepted 10 October 2002

Abstract

Recent work performed at DERA (now QinetiQ) has shown how accelerating rate calorimetry (ARC) can be used to obtain time to maximum rate curves using larger samples of energetic materials. The use of larger samples reduces the influence of thermal inertia, permitting experimental data to be gathered at temperatures closer to those likely to be encountered during manufacture, transportation or storage of an explosive device. However, in many cases, extrapolation of the time to maximum rate curve will still be necessary. Because of its low detection limit compared to the ARC, heat conduction calorimetry can be used to obtain data points at, or below, the region where an explosive system might exceed its temperature of no return and undergo a thermal explosion.

Paired ARC and heat conduction calorimetry experiments have been conducted on some energetic material samples to explore this possibility further. Examples of where both agreement and disagreement are found between the two techniques are reported and the significance of these discussed. Ways in which combining ARC and heat conduction calorimetry experiments can enhance, complement and validate the results obtained from each technique are examined.

Keywords: Heat conduction calorimetry; Propellants; Adiabatic calorimetry

---

1. Introduction and background

Assessment of the safety of munitions when subjected to extreme environmental conditions is of great importance to the British Ministry of Defence, justifying the expenditure of considerable time and effort on safety trials. However, comprehensive hazard trials are very expensive, especially if they need to be repeated, for example, in response to a minor change in the manufacturing process for a qualified system. It is therefore highly desirable to obtain an improved general understanding of the physical and chemical processes involved in thermal runaway to compliment and enhance the existing tests and possibly allow a reduction in the number of expensive large scale tests required to assess cook-off safety hazards accurately. An approach which may help to address this requirement is the application of calorimetric tests such as accelerating rate calorimetry (ARC) and heat conduction calorimetry.

The ARC is an automated laboratory instrument which experimentally determines the temperature, pressure and time relationships of exothermic reactions in a confined, adiabatic environment. It has been

---

☆ This paper was presented at the 3rd International Symposium on the Heat Flow Calorimetry of Energetic Materials, French Lick Springs, IN, USA, 8–10 April 2002.

* Corresponding author. Fax: +44-1959-516041.
E-mail address: pfbunyan@qinetiq.com (P.F. Bunyan).

0040-6031/03/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0040-6031(03)00051-0

used extensively by the chemical industry to evaluate the risk of thermal explosions in containers of self heating materials under a variety of conditions. In principal, we can regard a weapon such as a rocket motor as a system of this type and therefore suitable for study by ARC. However, the extremely high energy released during the decomposition of military explosives will mean that special attention must be paid to certain aspects of ARC technique and data handling which were of less importance, and could be ignored, when systems containing less energetic materials have been studied. It has been reported that, in order to get fully controlled runaway curves from explosives and propellants, far smaller sample masses had to be used than would be satisfactory for less energetic systems [1]. Thermal inertia (ϕ) values were therefore rather high, leading to a reduced volume of data and higher onset temperature detection thresholds. This was undesirable, since the results had to be extrapolated over a relatively large temperature range.

However, it is possible to record the early part of the runaway reaction using a larger energetic material sample, before ignition occurs, under far more favourable conditions (lower ϕ, lower onset temperature, etc.). In many cases involving decomposition reactions in highly energetic materials of high activation energy, a plot of ln(time to maximum rate, ϕ_{m}) versus $1/T$ exhibits a straight line relationship. However, a plot of ln(incorrect ϕ_{m}) versus $1/T$ yields a positive curve if the assumed time of maximum rate is longer than the true figure, or a negative curve if the assumed time of maximum rate is shorter than the true figure. This has been demonstrated experimentally using a variety of highly exothermic systems [2]. It follows that it would be possible to obtain valid time to maximum rate plots, even in the absence of an experimentally measured time of maximum rate by trial and error, by plotting a series of time to maximum rate curves for different assumed times of maximum rates and then choosing the straightest plot as the correct one. It has been reported that a valid estimate of what the time to maximum rate would have been if no transition to ignition reaction had intervened can be obtained and used to construct valid time to maximum rate plots using this iterative approach [2].

With the use of this technique, it is possible to obtain quantitative adiabatic calorimetry data commencing at lower temperatures than in the past. However, the technique is still only moderately sensitive and in many cases some extrapolation will be required to describe self heating behaviour of many explosive containing systems at the temperature of interest.

If a straight line law is seen from the time to maximum rate plot, obviously it can be extrapolated. However, a number of physical or chemical processes could potentially intervene at intermediate temperatures which might invalidate the extrapolated values, e.g. phase transitions, loss of volatiles in open systems, autocatalysis by volatile products which are lost from porous systems, domination of the heat generation in the system at low temperatures by a reaction of low activation energy and at high temperatures by a reaction of high activation energy. These have been discussed by Whitmore and Wilberforce [3].

Therefore, in order to have confidence in the extrapolated ARC result, its validity should be checked by critical experiment, at, or below the temperature of interest.

A heat conduction calorimeter such as the thermal activity monitor (TAM) measures low levels of heat generated by a thermally active material under isothermal conditions. This technique has a far lower detection threshold than the ARC. The sensitivity and reproducibility of the TAM technique has been investigated in detail by Wilker et al. [4] and shown to be capable of quantifying heat generation rates of less than a microwatt. In practical terms this means that the heat generated by nitrate ester explosive materials, for example, can be monitored at temperatures well below those that might cause critical storage temperatures to be approached. It is therefore ideally suited to validating extrapolated ARC time to maximum rate plots.

Self heat rate and heat generation rate can be easily interconverted, although direct comparison of experimental ARC and HFC data is often not possible in practice, since the differences in detection limits associated with the two techniques mean that data collection temperature ranges, used to study the same material, rarely overlap.

The strengths and weaknesses of the TAM and the ARC are to some extent mutually exclusive. Unlike the ARC, the TAM is unable to reach higher temperatures or record entire explosive decomposition reactions. However, its low detection limit makes it ideal for single point checks at moderate temperatures.

This paper describes combined studies where both ARC and TAM techniques have been used to examine identical materials. One example where the extrapolation appears valid and one example where the extrapolation clearly fails, are described in detail.

2. Theory and calculations

Providing the appearance of the experimental time to maximum rate curve is a straight line, Eq. (1) can be solved and used to predict the time to maximum rate at any other temperature [5].

$$\ln(\theta_{\mathrm{m}}) = -\ln A + \frac{E}{R}\left(\frac{1}{T}\right) \tag{1}$$

where θ_{m} is the time to maximum rate at temperature T, A the pre exponential factor, E the activation energy, R the gas constant, T the absolute temperature.

A prediction of expected heat generation rate at temperature T can be obtained using Eq. (2), as described by Wilberforce [6].

$$q = \frac{RT^2 C_{\mathrm{v}}}{\theta_{\mathrm{m}} E} \tag{2}$$

where q is the heat generation rate at temperature T, C_{v} the specific heat capacity.

Conversely, if heat generation rate and activation energy are measured from heat conduction calorimetry experiments an adiabatic time to maximum rate can be estimated from microcalorimetry data, by rearrangement of Eq. (2) to give Eq. (3).

$$\theta_{\mathrm{m}} = \frac{RT^2 C_{\mathrm{v}}}{qE} \tag{3}$$

From a series of microcalorimetry studies conducted at different temperatures, a series of temperature/time to maximum rate data pairs can be generated and an analogous equation to one obtained from the regression line of a plot of ln(time to maximum rate) versus reciprocal of absolute temperature.

Obviously the two time to maximum rate plots would coincide if the reaction responsible for the heat generation process followed the same chemical mechanism over both ARC and TAM temperature ranges and obeys an Arrhenius law variation of rate with temperature. It follows that a single TAM experimental result can be compared with a result calculated from extrapolated ARC data. If the extrapolation is valid, the expected and observed rates should be comparable.

Once an estimate of heat generation rate of the self heating material has been made and validated, whether or not a system incorporating it will be stable will depend on the environment it experiences. The heat generation rate will be one variable which, when considered along with other relevant parameters (including heat loss characteristics of the container, temperature of the surroundings, specific heat capacity and in the case of solids, thermal conductivity) will allow critical conditions to be assigned.

3. Experimentation and results

An ARC experiment was conducted on each of the selected materials. After estimating the time of maximum rate iteratively [2], a time to maximum rate plot of ln(time to maximum rate) versus the reciprocal of the absolute temperature, was constructed. The adiabatic time to maximum rate at a lower temperature, within the operating range of the TAM, was calculated by extrapolation and an expected heat generation rate at this temperature calculated using Eq. (2).

Heat generation was measured experimentally at this lower temperature by microcalorimetry and the rate observed compared with the rate anticipated from the earlier ARC experiment. One example where the extrapolation appears valid (a double base rocket propellant, Section 3.1) and one example where the extrapolation appears invalid (ammonium dinitramide (ADN), Section 3.2) are described in detail. Results from all materials studied are summarised in Table 1.

3.1. *Example 1—double base rocket propellant*

The first example uses a double base rocket propellant containing; nitrocellulose 53%, nitroglycerine 42.2%, 2-nitrodiphenylamine 2.0% and dibutylphthallate 2.8%. Specific heat capacity was determined by DSC at 80 °C to be 1.58 J $(\mathrm{g}^{-1}\,\mathrm{K}^{-1})$.

A scanning heat-wait-search (HWS) ARC experiment was performed. Experimental conditions were: sample mass: 4.6867 g, Bomb type: 2.54 cm diameter spherical titanium, initial temperature: 100 °C, final temperature: 140 °C, self heat detection threshold:

Table 1
Comparison of extrapolated ARC data with 80 °C microcalorimetry experiments

ARC experiment	Predicted rate at moderate temperature (ARC[a]) (μW g^{-1})	Mean experimentally observed rate at moderate temperature (heat conduction calorimetry) (μW g^{-1})
Run 333 (PolyNIMMO)[b]	$4.79 < q < 4.95$[c]	9.0
Run 340 (PolyGLYN)[b]	$13.44 < q < 14.03$[c]	21.2
Run 344 (GAP)[b]	$0.34 < q < 0.38$[c]	1.64
Run 348 (single base propellant)[b]	$35.07 < q < 35.97$[c]	9.2
Run 350 (double base propellant)[b]	$15.1 < q < 16.4$[c]	16.4
Run 392 (ammonium dinitramide)[d]	$1925 < q < 2304$[c]	2.0

[a] Predicted self heat rate at lower temperature obtained by extrapolation of time to maximum rate plot from low ϕ ARC experiment. This can then be converted to heat generation rate using Eq. (2).

[b] Moderate temperature = 80 °C.

[c] Calculated range for expected heat generation rates calculated by extrapolation of time to maximum rate plots (95% confidence interval).

[d] Moderate temperature = 70 °C.

0.015 °C min^{-1}, step: 3 °C, wait time: 10 min, data step temperature: 1 °C, thermal inertia: 2.32, atmosphere: nitrogen.

The raw data plot of temperature versus time is shown in Fig. 1.

A time of maximum rate was estimated iteratively as described in [2] and used to construct a ϕ corrected time to maximum rate plot (Fig. 2).

Extrapolating the equation of the best fitting straight line to a starting temperature of 353.15 K gives an estimated ln(adiabatic time to maximum rate) of 9.24 ± 0.04 ln(minutes), indicating an expected heat generation rate in the range $15.1 < q < 16.4\,\mu$W g^{-1} at 80 °C.

A 2.4638 g sample of the double base propellant was sealed in an atmosphere of nitrogen in a 3 cm^3 glass ampoule, lowered into the detection region of the TAM and the heat generation resulting from the exothermic decomposition reactions monitored until a constant signal was observed. The TAM thermostat was set at 80 °C. A plot of heat generation rate and total heat evolved against time are illustrated in

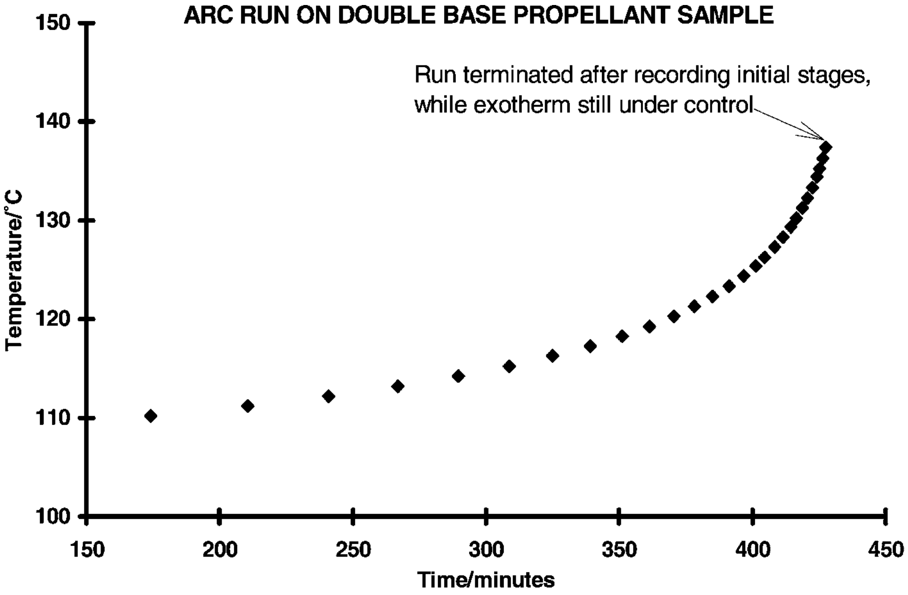

Fig. 1. Double base propellant—adiabatic temperature vs. time curve.

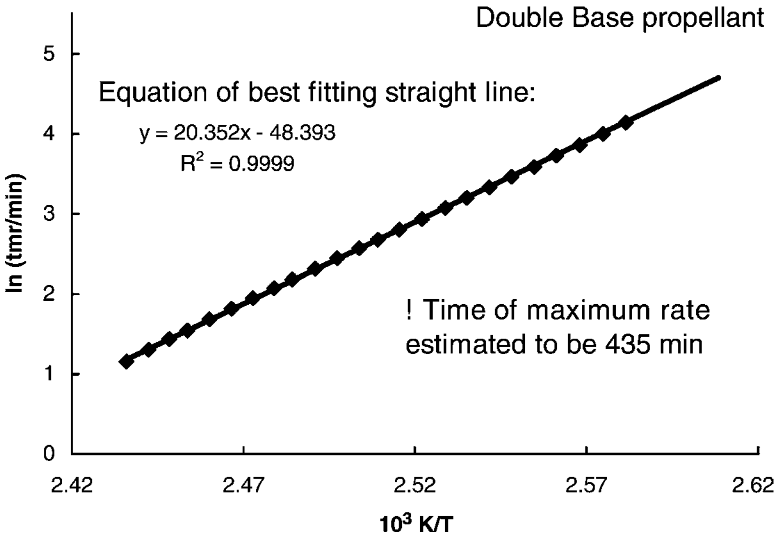

Fig. 2. Double base propellant—time to maximum rate plot.

Fig. 3. It can be seen that, once thermal equilibrium had been achieved, a reasonably constant heat generation rate of 16.4 μW g^{-1} was recorded, i.e. very close to the value expected by calculation from the ARC experiment.

3.2. Example 2—ammonium dinitramide

The second example used ammonium dinitramide (ADN). This has been proposed for use as an oxidiser in high energy, low signature propellant compositions.

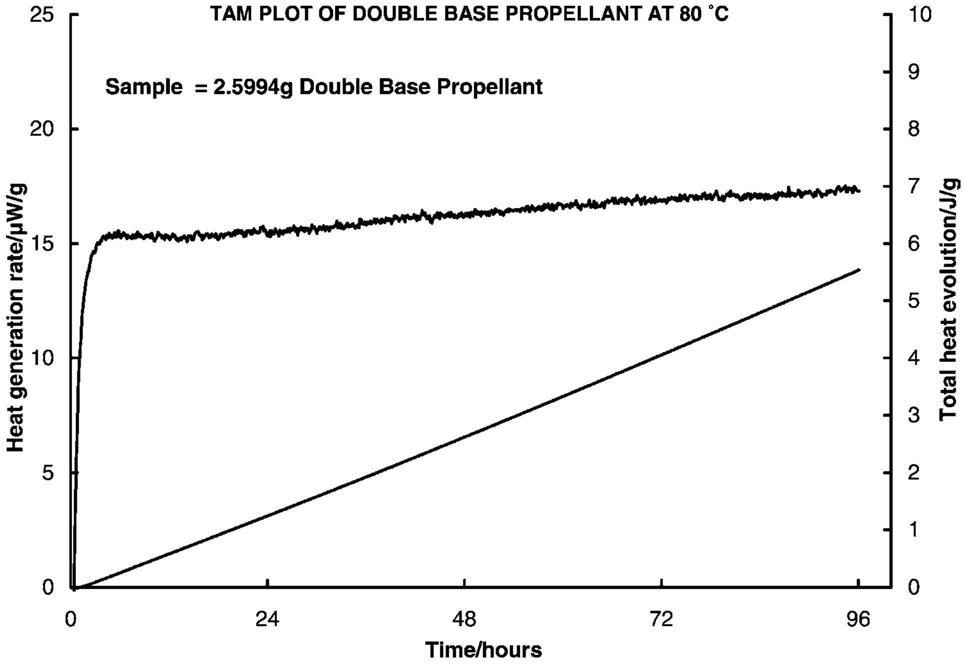

Fig. 3. Double base propellant—heat generation at 80 °C by heat conduction calorimetry.

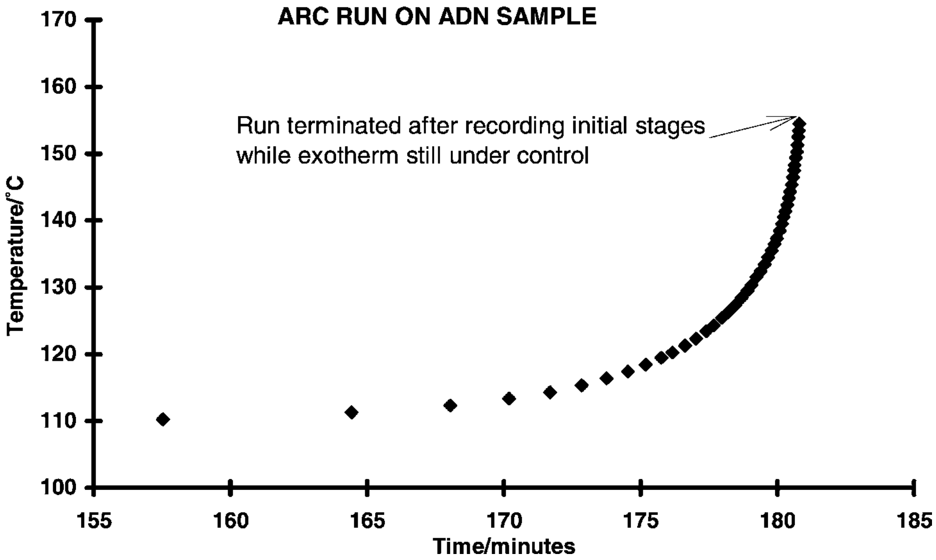

Fig. 4. Ammonium dinitramide—adiabatic temperature vs. time curve.

Specific heat capacity was determined by DSC at 70 °C to be 1.4 J (g^{-1} K^{-1}). TAM experiments were conducted at a lower temperature of 70 °C This was to avoid any complications introduced by working at temperatures close to the melting point of ADN and also because ARC studies suggested that heat generation at 80 °C might exceed the measuring range of the TAM.

A scanning heat-wait-search (HWS) ARC experiment was performed. Experimental conditions were as for the previous example, except that sample mass was 0.3623 g, initial temperature was 100 °C, final temperature was 155 °C and thermal inertia was 20.06.

The raw data plot of temperature versus time is shown in Fig. 4.

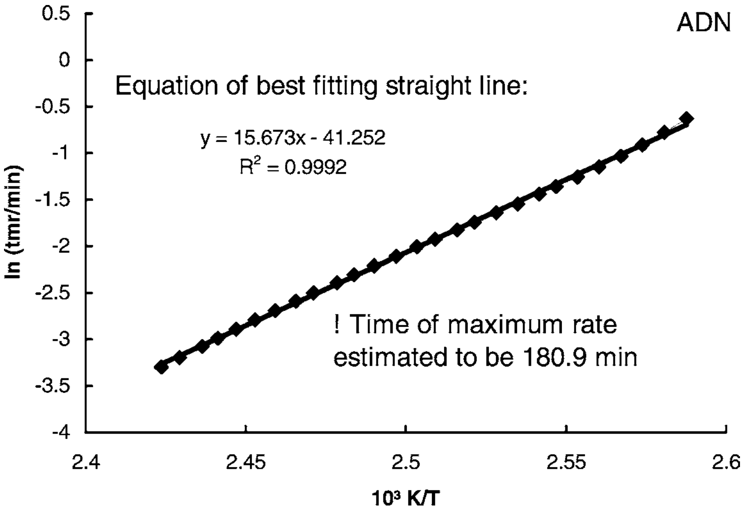

Fig. 5. Ammonium dinitramide—time to maximum rate plot.

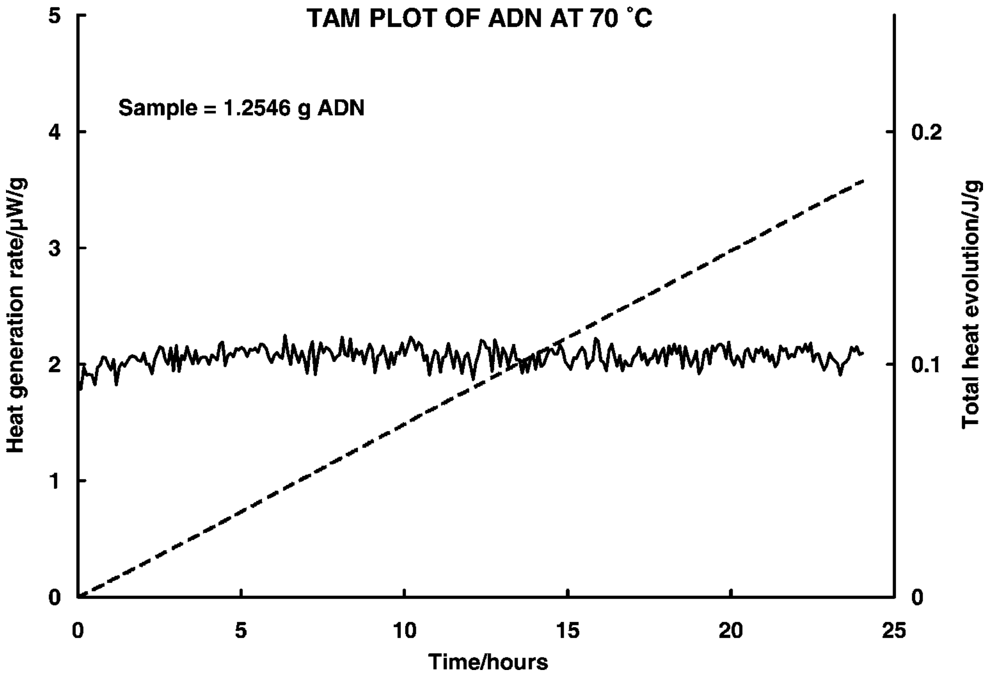

Fig. 6. Ammonium dinitramide—heat generation at 70 °C by heat conduction calorimetry.

A time of maximum rate was estimated iteratively [2] and used to construct a ϕ corrected time to maximum rate plot (Fig. 5).

Extrapolating the equation of the best fitting straight line gives an estimated ln(adiabatic time to maximum rate) of 4.42 ± 0.09 ln(minutes), indicating an extremely high expected heat generation rate in the range $1925 < q < 2304\,\mu\text{W g}^{-1}$ at only 70 °C.

A 1.2546 g sample of ammonium dinitramide was sealed in an atmosphere of nitrogen in a $3\,\text{cm}^3$ glass ampoule, lowered into the detection region of the TAM and the heat generation rate resulting from the exothermic decomposition reactions monitored until greater than $0.5\,\text{J g}^{-1}$ total heat energy had been generated. The TAM thermostat was set at 70 °C. A plot of heat generation rate and total heat evolved against time are illustrated in Fig. 6. It can be seen that, once thermal equilibrium had been achieved, a reasonably constant heat generation rate of $2\,\mu\text{W g}^{-1}$ was recorded, i.e. around 1000 times less than anticipated by calculation from the corresponding ARC experiment! Note that, if the original high prediction obtained using the ARC had been confirmed, it is difficult to see how this material could ever be considered for use as a propellant ingredient for service use!

3.3. *Other energetic materials examined*

Three energetic, rubbery binders, poly(3-nitratomethyl-3-methyloxetane) (PolyNIMMO), poly(glycidylnitrate) (PolyGLYN) and glydidyl azide polymer (GAP) and a single base gun propellant, nitrocellulose 98.5%, diphenylamine 0.85–1.5%, calcium carbonate 0.2–0.6% and graphite glaze 0.1–0.3%, were also studied by ARC and heat conduction calorimetry, employing a similar procedure to that described for the double base rocket propellant and ADN. Results are summarised, along with those from the double base propellant and ADN, in Table 1.

4. General discussion

In the case of all of the nitrate ester containing materials studied—both traditional propellants and new energetic binders, the results expected by calculation from ARC data and those found experimentally by heat conduction calorimetry, while not agreeing exactly, are of similar magnitude.

Although it is obviously better to look at the temperature of interest directly, this may not always be possible, e.g. if the relevant temperature is above 90 °C, but below the detection region of the ARC. In these cases, a decision has to be made as to whether a value for heat generation calculated by extrapolation is accurate enough to permit a useful decision about whether the system will be stable or not under designated environmental conditions.

If the critical extrapolation test survives to below that of the conditions of interest, the calculated heat generation rate under those conditions may be used with greater confidence in calculations to specify critical conditions. Just how close the agreement must be between expected and observed results at that temperature for the description to be judged valid will inevitably be a subjective decision based on experience and will depend on the perceived seriousness of a runaway and how large safety margins are deemed acceptable.

An example of where agreement is not found is provided by ADN where the observed heat generation rate measured at 70 °C by microcalorimetry is over two-orders of magnitude smaller than anticipated by calculation from the ARC experiment conducted at elevated temperature and well outside the range that could be accounted for by experimental error. In this case, examination of the DSC curve of ADN points to a likely explanation (Fig. 7). It can be seen that ADN melts between 90 and 100 °C and the discrepancy between ARC and HFC is consistent with a different, faster decomposition mechanism when ADN is molten compared to the crystalline material.

Obviously, the poor thermal stability of ADN above 80 °C is not ideal and if an alternative smoke-free, high energy oxidant was available it would be preferable to use it. However, there are only very few alternatives to ADN for use as oxidants in high energy/low smoke propellants, and all have limitations at least as inconvenient as the high temperature stability of ADN. If it is considered that the advantages of ADN warrant its use, it can at least be used with an understanding of the operational constraints its use would impose, i.e. the risk may be managed, if properly understood. Obviously data gathered at temperatures below 80 °C would be relevant for 'normal' lifetime prediction, while

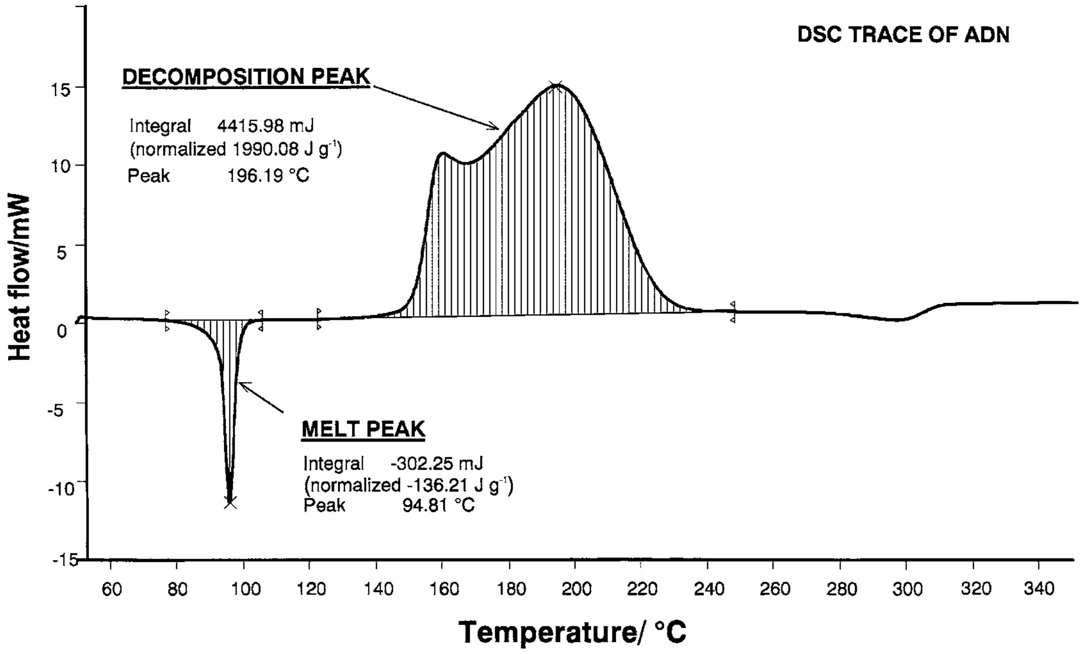

Fig. 7. Ammonium dinitramide—differential scanning calorimetry trace.

assessing what might happen in the event of accidental heating, for example resulting from a nearby fire, would require the use of experimental data gathered above 90 °C.

5. Conclusions and recommendations

The self heating characteristics of a number of energetic materials have been described using the techniques of accelerating rate calorimetry and microcalorimetry in combination. It has been shown that the two techniques are largely complimentary and that their strengths and weaknesses are mutually exclusive. Although ARC and TAM data can be interconverted (i.e. self heat rate to/from time to maximum rate), direct comparison of experimental data gained over the same temperature range is often not possible, due to these techniques having very different sensitivities. However, once a general description of the self heating characteristics of an energetic material has been made using the ARC, the high sensitivity of the TAM makes it an ideal way to confirm or deny the validity of extrapolating the ARC data to lower temperatures.

All of the nitrate ester energetic materials studied here show a sufficient level of agreement between results from the two techniques to be of some practical use. It seems reasonable to assume that the heat generating decomposition reactions may be described by a single Arrhenius equation with sufficient accuracy to allow practical hazard assessments to be made over the temperature range studied experimentally. Obviously it would be unwise to assume that an approximate straight line relationship would be valid at temperatures above or below those where any experimental measurements have been taken by either technique. For example, it has been reported that many nitrate ester based propellant materials show a characteristic break in the Arrhenius curve at around 55 °C [7]. This indicates some change in decomposition mechanism resulting in a lower apparent activation energy as ambient temperatures are approached than would be measured by experiments performed at elevated temperatures.

In contrast, in the case of ADN, comparison of heat generation expected from extrapolated ARC studies and microcalorimetric measurements made at 70 °C show that the ARC data clearly cannot be extrapolated to lower temperatures. The reason for this appears to be the intervening melting transition causing a mechanism change between 80 and 90 °C. Obviously data gathered at temperatures below 80 °C would be relevant for ‘normal’ lifetime prediction, while assessing what might happen in the event of accidental heating; for example resulting from a nearby fire, would require the use of experimental data gathered above 90 °C.

It is recommended that data obtained from high temperature ARC experiments should be validated by the use of heat conduction calorimetry experiments conducted at temperatures below the temperature where the self heating hazards of the system of interest are being considered.

Acknowledgements

This work was supported and funded by UK MOD (DOSG).

References

[1] P.F. Bunyan, D.A. Tod, G. Kavanagh, Characterisation of Thermal Runaway Reactions in Energetic Solid Materials Using Accelerating Rate Calorimetry, in: Proceedings of the 30th International Conference of ICT, Paper P62, Karlsruhe, Germany, 29 June to 2 July 1999.

[2] P.F. Bunyan, D.A. Tod, Accelerating Rate Calorimetry Experiments on Energetic Materials: Obtaining Time to Maximum Rate Plots on Larger Samples, in: Proceedings of the 31st International Conference of ICT, Paper V4, Karlsruhe, Germany, 27–30 June 2000.

[3] M.W. Whitmore, J.K. Wilberforce, J. Loss Prev. Process Ind. 6 (2) (1993) 95.

[4] S. Wilker, U. Ticmanis, G. Pantel, Detailed Investigation of Sensitivity and Reproducibility of Heat Flow Calorimetry, in: Proceedings of the 11th Symposium on Chem. Probl. Connected Stabil. Explos., Sweden, 1998.

[5] D.I. Townsend, J.C. Tou, Thermochim. Acta 37 (1980) 1.

[6] J.K. Wilberforce, J. Therm. Anal. 25 (1982) 593.

[7] U. Ticmanis, S. Wilker, G. Pantel, M. Kaiser, P. Guillaume, C. Bales, N. van der Meer, Principles of a STANAG for the Estimation of the Chemical Stability of Propellants by Heat Flow Calorimetry, in: Proceedings of the 31st International Conference of ICT, Paper V2, Karlsruhe, Germany, 27–30 June 2000.