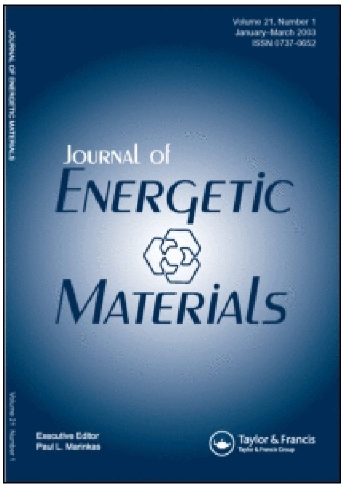

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The Thermal Decomposition of 2,5-Dipicryl-1,3,4-oxadiazole, near its Ignition Temperature : an Isothermal DSC Study

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ABSTRACT

2,5-Dipicryl-1,3,4-oxadiazole (DPO) is a thermally stable, high impulse shock sensitive explosive, which decomposes in the solid state at a rate easily followed by isothermal differential scanning calorimetry between 575 K (302°C) and 598 K (325° C). The α-t plots follow a typical sigmoidal profile and the kinetic data has been analysed in terms of the two standard rate laws which characterise many sigmoidal nucleation, growth and decomposition reactions, viz. the Prout-Tompkins rate law and the Avrami-Erofe'ev rate law. Both give an excellent description of the reaction kinetics over the approximate range $0.08 < \alpha < 0.80$, but the apparent reaction order associated with Avrami-Erofe'ev kinetics is temperature dependent. An Arrhenius plot based on Prout-Tompkins kinetics suggests that the thermal decomposition of DPO proceeds with an activation energy of 218 kJ mol $^{-1}$ and a pre-exponential, ln A(s^{-1}), of 39.83, while that based on Avrami-Erofe'ev kinetic data yields an activation

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energy of 184 kJ mol^{-1} and ln $A(s^{-1})$ of 30.92. Ramifications of these results are discussed.

INTRODUCTION

2,5-Dipicryl-1,3,4-oxadiazole (DPO) and 2,2',4,4',6,6'-hexanitrostilbene (HNS) are structurally similar in that they each contain two picryl groups linked by a degree of conjugation; in the case of DPO, the linkage is through a symmetrical heteroaromatic ring; in the case of HNS, it is a simple olefinic linkage. Both are thermally very stable compounds and they both decompose without melting at temperatures in excess of 300°C. Because there has been growing interest in the use of explosive materials of high thermal stability, it was decided to investigate the kinetics of the thermal decomposition of each of these compounds in some detail. The results of the study on HNS have already been published [3] ; the present report details those for DPO and stresses the mechanistic implications of such a study with regard to solid state organic thermal decompositions, in general.

EXPERIMENTAL

Materials

DPO was synthesised by Sitzmann's method, from the product of the hydrazinolysis of trinitrobenzoyl chloride [1]. It is a fine, pale yellow solid (ex acetone), which decomposes without melting above 320°C, the upper limit of our melting point apparatus (lit. m.p. 335°C) [1]. Its ^{1}H-nmr spectrum in DMSO-d_6 consisted of a single peak, at δ 9.38 ppm., (lit. 9.52 ppm.) [1].

Thermal Analysis

All DSC measurements were carried out under nitrogen (20-25 mL min^{-1} flow rate) using a Perkin Elmer DSC Model 2C: samples, approx. 0.5 mg, were weighed into Al sample pans and covered with an Al lid (not crimped), and runs carried out, non-isothermally as well as isothermally, following previously described methods [3,4]. The kinetic data were analysed using standard spreadsheet techniques.

In the non-isothermal runs it was found that, at high heating rates (> 20 °C min^{-1}), even small samples (ca. 0.2 mg) of DPO were prone to self-heating at temperatures above the decomposition temperature; this was a consequence of the speed of the decomposition reaction and its strongly exothermic nature [5] In isothermal runs above 605 K, similar problems arose, especially when the reaction proceeded beyond the 20 % reaction point.

TGA/DTA measurements were carried out simultaneously on a Stanton Redcroft / Polymer Laboratories [U.K.] Simultaneous Thermal Analyser, Model STA-1500 (nitrogen atmosphere), to complement the DSC studies.

RESULTS AND DISCUSSION

The non-isothermal DSC trace of DPO consists of just a very simple, sharp exotherm. At a heating rate of 5 K min^{-1} (under nitrogen), decomposition commences at ca. 590 K, with an (extrapolated) T_{onset} of 604 K and T_{max} of 607.5 K, results which are confirmed by combined DTA/TGA. The total heat output associated with this exotherm is 2240 ± 105 mJ mg^{-1} (from data obtained at several different heating rates).

Preliminary experiments indicated that the thermal decomposition of DPO could be followed easily over the whole decomposition range by isothermal DSC between 575 and 598 K.

The output of the isothermal DSC trace from the thermal decomposition of DPO at 589.8 K is presented in Table 1 and Fig. 1. It is typical of that obtained from other runs over the range of temperatures studied. The heat output for the complete reaction at 589.8 K was found, for this particular run, to be 2017 mJ mg^{-1}, a figure at the lower end of that for other runs, 2118 ± 105 mJ mg^{-1}. This total heat output is similar to that from the non-isothermal study, outlined above.

If one assumes that the heat output arises from a single set of processes operating throughout the whole reaction, then the sigmoidal plot of heat output (representing the extent of reaction or the fractional decomposition of reactant, α) vs. time (t) is typical of many α-t plots obtained in solid state reactions [6-10].

Isothermal TGA studies, on 2 mg samples, indicate that 90 ± 3 % mass loss (uncorr.) occurs over the period of the thermal decomposition; the shape of the mass loss (δm) - t profile is also sigmoidal and very similar to, if not identical with, the α-t plot from isothermal DSC. The residue from the TGA studies was found to be a coherent char, more likely from a decomposition from the solid state than from a melt.

The analysis of the kinetic processes leading to a sigmoidal α-t plot have been described in detail, many times [6-8].

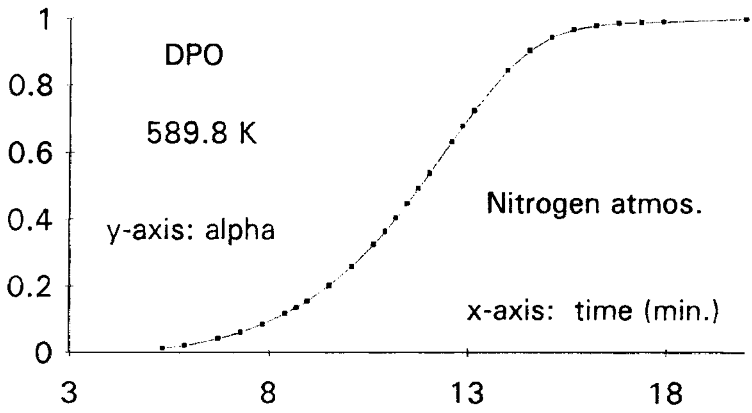

Fig. 1 The α-t profile for the thermal decomposition of DPO at 589.8 K, under flowing nitrogen.

For the solid state reaction, A(s) → products, there are at least three major stages and the actual shape of the α-t profile will depend on the particular rate law governing the distribution and reactivity of the reactant nuclei in the host matrix [3b]. These stages involve

(1) prenucleation, which leads to the formation of a large number of sites of high free energy, from which reaction initially proceeds [6-8],

(2) the major reaction domain, where the decomposition proceeds rapidly and usually gives the most reliable description of the global kinetics (when one is relying on data from thermal analysis), and

TABLE 1 : The Thermal Output from the Isothermal Decomposition of DPO, 2,5-Dipicryl-1,3,4-oxadiazole at 589.8 K, under flowing nitrogen.

Time (min.)	Partial heat evolved (mJ mg^{-1})	Alpha
5.88	39	0.0195
6.72	80	0.0396
7.28	119	0.0589
7.84	170	0.0841
8.40	233	0.1156
8.68	270	0.1340
8.96	312	0.1546
9.52	408	0.2023
10.08	522	0.2588
10.64	656	0.3253
10.92	732	0.3630
11.20	814	0.4034
11.48	901	0.4467
11.76	993	0.4922
12.04	1086	0.5386
12.60	1274	0.6318
12.88	1367	0.6777
13.16	1458	0.7228
13.44	1545	0.7661

TABLE 1 (cont.)

Time (min.)	Partial heat evolved (mJ mg^{-1})	Alpha
14.00	1703	0.8443
14.56	1823	0.9040
15.12	1904	0.9437
25.00	2017	1.0000

(3) the deceleratory reaction time-domain, where the bulk matrix supporting the original reactant nuclei has probably altered or even disappeared although the immediate molecular environment of the remaining reactant molecules may still be intact.

Prenucleation kinetic studies often need to be accompanied by a direct visual technique (eg. microscopy) to identify what is happening [6-8] and it is from the second stage, from ca. $0.15 < \alpha < 0.85$, that the most reliable global kinetics can often be determined when one has to rely on data from thermal analysis.

Of the various kinetic models commonly encountered in solid state thermal decomposition reactions of inorganic substrates [6-10], two have a sigmoidal α-t line shape, the Prout-Tompkins relationship,

$$d(\alpha)/dt = k'\alpha(1-\alpha) \qquad \text{(Eq.1 a)}$$

or, in integrated form,

$$\ln [\alpha / (1 - \alpha)] = k' (t - t_{0.5}) \qquad \text{(Eq 1 b)}$$

(where $t_{0.5}$ is the reference time at $\alpha = 0.5$)

and the Avrami-Erofe'ev relationship,

$$- \ln (1 - \alpha) = (k'' t)^n \qquad \text{(Eq. 2 a)}$$

or

$$\ln (\ln [1/(1 - \alpha)]) = n \ln k'' + n \ln t \qquad \text{(Eq. 2b).}$$

(where n is a reaction order term; it is the sum of λ, the number of dimensions in which a potential reaction site or nucleus grows as reaction proceeds, and β, the number of kinetic steps required for the formation of the growing nucleus responsible for reaction at that site [8]).

The development of the underlying theory behind these equations comes from a long and detailed study of the thermal decomposition of crystalline, inorganic salts in the solid state [6-8] In these studies, it was found that the advancing reaction site can be gradually modified by the formation of solid products, by the interaction with interfering products and by the superposition or assimilation of another, adjacent advancing reaction site, all of which can result in a complex, heterogenous matrix from which subsequent reaction proceeds; it is from the interaction of these branching nuclei and from their growth, agglomeration and decay that the various α-t profiles manifest themselves [6-8]. These concepts should have a counterpart in the solid state thermal decomposition of organic compounds [11,12], although, as far as the present authors can ascertain, there has been little or no attempt to look closely at, to systematise or to analyse the experimental data on organic compounds with any degree of sophistication [13-15]; this arises partly because most organic compounds melt prior to undergoing thermal decomposition and partly because there has only been limited interest in the area [11,14,15].

Using the DSC data in Table 1, one finds that a Prout-Tompkins plot of $\ln [\alpha/(1 - \alpha)]$ vs. t for the thermal decomposition data from DPO at 589.8 K is linear for $0.08 < \alpha < 0.80$ with coefficient of determination, r^2, of 0.997. The slope of this plot, 0.6325 min.^{-1}, represents the rate constant, k', for this reaction. Similar linear plots are obtained over the temperature range studied, 574.8 to 604.8 K, yielding data summarised in Table 2.

Using the same α-t data and presenting it in the form of the log-log (Avrami-Erofe'ev) relationship, viz., $\ln (-\ln [1-\alpha])$ vs. $\ln t$, yields a linear trace ($r^2 = 0.999$) over the range $0.05 < \alpha < 0.90$. Analysis of this trace in terms of Eq. 2b gives a slope, n, of 5.2_4 and corresponding intercept, $n \ln k''$ (min.^{-1}), of -13.24, which in turn gives a value of k'', 0.0798 (min.^{-1}). Again, linear plots are obtained for all of the plots over the temperature range studied, yielding data summarised in Table 2. However, it was observed that the values of the slope, n, did vary with temperature - from a value of 4.5_1 for runs at 574.8 K to 5.7_8 at 597.8 K - suggesting that either the reaction is kinetically complex (the numerical value of β altering as temperature increases) or considerable structural disruption and reorganisation around the decomposing molecules is taking place (thus altering the value of λ); alternatively, both effects may be operating in concert. This is not unreasonable as one would expect that once decomposition of a complex molecule such as DPO commences, marked changes to the crystalline lattice due to molecular volume changes and the generation of potentially gaseous

Table 2. Kinetics of the thermal decomposition of DPO (574.8 K to 604.8 K) as analysed by the Prout-Tompkins and the Avrami-Erofe'ev approaches.

	Prout -Tompkins	Avrami-Erofe'ev	
Temp., (K)	k', min^{-1}	k", min^{-1}	Reaction Order, n
574.8	0.2027	0.0301	4.505
577.9	0.2397	0.0369	4.589
579.9	0.2982	0.0419	4.443
584.7	0.4156	0.0586	4.601
589.8	0.6325	0.0798	5.242
594.8	0.904	0.1107	5.518
597.8	1.1404	0.1314	5.782
604.8¶	2.2413	0.1925	8.08

¶ Self-heating observed at 604.8 K; kinetics followed for $\alpha < 0.19$, only. This result was not used in the determination of the Arrhenius parameters; however, it does illustrate how dramatically the reaction order appears to change in the Avrami-Erofe'ev analysis.

Prout-Tompkins Arrhenius parameters from the plot of ln k (min^{-1}) vs. (1 / T) :

Activation energy: 218 kJ mol^{-1}, ln A (s^{-1}): 39.83.

Coefficient of determination: 0.998.

Avrami-Erofe'ev Arrhenius parameters from the plot of ln k (min^{-1}) vs. (1 / T) :

Activation energy: 184 kJ mol^{-1}, ln A (s^{-1}): 30.92.

Coefficient of determination: 0.999.

products would ensue. The rate constant, k", is affected only by Arrhenius factors, while the reaction order is affected by changes to λ and β with temperature [8].

Both sets of results follow a linear Arrhenius, (ln k vs. 1/T) relationship. If the thermal decomposition of DPO follows the Prout-Tompkins rate law, one obtains an activation energy, E*, of 218 kJ mol^{-1} and Arrhenius preexponential, ln $A(s^{-1})$, of 39.83; if the thermal decomposition follows an Avrami-Erofe'ev rate law, one obtains an activation energy, E*, of 184 kJ mol^{-1} and Arrhenius preexponential, ln $A(s^{-1})$, of 30.92. Both these sets of values are kinetically plausible [8] but whether one can relate either of the numerical values of E* and ln A to a specific rate-controlling bond rupture at the molecular level is open to debate; the specialist exponents of solid state reaction kinetics are by no means convinced that the data can be interpreted unequivocally in this way [8]. While the energy of activation, E*, should be related to bond breaking and enthalpy changes in the transition state of the activated complex in the thermal decomposition process, the Arrhenius preexponential factor, A or ln A, and the reaction order, n, should reflect features associated with microcrystalline structure of the decomposing substrate, the changes therein and the entropy changes. It was against this background that experimentally-observed kinetic processes were rationalised in inorganic, solid state thermal decomposition reactions and it is upon the framework developed there that the classification of these reaction pathways has been clarified. Unfortunately, in the present study, it was not possible to look and identify at the gaseous products of the decomposition, with the facilities at the authors' disposal.

What is important, as far as DPO is concerned at this stage, is that the kinetic description of the data (Table 2) gives one a handle on the overall decomposition process and enables one to model global effects, provided that the correct form of the rate equation and the corresponding kinetic data are used in conjunction with any calculations.

If, in fact, the thermal decomposition of DPO is really controlled by processes described by Avrami-Erofe'ev kinetics, then its activation energy, 184 kJ mol^{-1}, is somewhat greater than that observed from HNS in the melt, 163 kJ mol^{-1} (where the reaction follows first order kinetics), but very similar to that for the solid state thermal decomposition of HNS, 178 kJ mol^{-1} (where the reaction follows Prout-Tompkins kinetics very satisfactorily, for $0.75 > \alpha > 0.25$) [16]. On the other hand, if the thermal decomposition of DPO is controlled by processes described by Prout-Tompkins' kinetics and the activation energy is some 30 kJ mol^{-1} greater, 218 kJ mol^{-1}, then the mechanistic interpretation, at the bond-making and bond-breaking level, is somewhat clouded.

The quandary as to the interpretation of the kinetic pathway by which DPO actually decomposes is similar to that relating to the thermal decomposition of tetryl, 3-aminotetryl, 3-AT, and 3,5-diaminotetryl, 3,5-DAT [17], as reported by Hutchison, Krishna Mohan and Millar [17].

They found that tetryl melted first, at 402 K, and then decomposed at temperatures above ca. 440 K. Its thermal decomposition followed the kinetic rate law

$$d(\alpha)/dt = k'\alpha(1-\alpha)$$

which they attributed to an (undefined) second order autocatalytic reaction, an equation which is kinetically (but not mechanistically) akin to the formal solid state Prout-Tompkins' equation. On the other hand, 3-AT and 3,5-DAT, at temperatures just below their respective melting points, decomposed following Avrami-Erofe'ev kinetics (n = 3 for 3-AT and n = 4 for 3,5-DAT); one presumes that, in each case, the substituted tetryls remained solids during the decomposition process although this may no longer be considered a prerequisite for a reaction to follow Avrami-Erofe'ev kinetics [14,15]. With DPO, the nature of the coherent char suggests that DPO does not melt during its thermal decomposition.

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REFERENCES

1. M.E. Sitzmann, *J. Energetic Mats.*, 6 129 (1988).
2. M. Kony, L. Montelli and D. Whelan, "An Initial Assessment of the Properties of 2,5-Dipicryl-1,3,4-oxadiazole (DPO), a Secondary Explosive with High Thermal Stability", Materials Research Laboratory Technical Report, MRL-TR-93-16 (1993).
3. a) D. J. Whelan, M. Maksacheff, B. Pletikapa and L.V. deYong, *J. Energetic Mats.*, 6 201 (1988).

b) D. J. Whelan, B. Pletikapa and M.R. Fitzgerald, *J. Energetic Mats.*, 7 133 (1989).

4. M.J. Kony, I.J. Dagley and D.J. Whelan, *J. Phys. Chem.*, 96 8001 (1992).
5. G.L. Batch and C.W. Macosko, *Thermochim. Acta*, 188 1 (1991).
6. P.W. M. Jacobs and F. C. Tompkins, "Classification and Theory of Solid Reactions" in W. E. Garner (Editor), *Chemistry of the Solid State*, Butterworth Scientific, London (1955) pp 184 - 213.
7. L. G. Harrison, "The Theory of Solid Phase Kinetics" in C. H. Bamford and C. F.H. Tipper (Editors), *Comprehensive Chemical Kinetics*, Elsevier, Amsterdam (1969), Vol. 2, Chapt. 5 esp. pp 377 - 404.
8. W.E. Brown, D. Dollimore and A. L. Galwey, "Reactions in the Solid State" in C. H. Bamford and C. F. H. Tipper (Editors), *Comprehensive Chemical Kinetics*, Elsevier, Amsterdam(1980), Vol. 22, Chapt. 3 and 4, esp. pp 55-58, 65-68, 84-89.
9. C. Rozycki and M. Maciejewski, *Thermochim. Acta*, 122 339 (1987).
10. J.H. Sharp, G.W. Brindley and B.N. Narahari Achar, *J. Am. Ceram. Soc*, 49 379 (1966).

    b) J.D. Hancock. and J.H. Sharp, *J. Amer. Ceram. Soc.*, 55 74 (1972).
11. C.E.H. Bawn, "The Decomposition of Organic Solids" in W. E. Garner (Editor), *Chemistry of the Solid State*, Butterworth Scientific, London (1955) pp 254-267.
12. J. Vaughan and L. Phillips, *J. Chem. Soc., London*, 1560 (1947).

13. A.K. Galwey and M.A. Mohammed, *Proc. Royal Soc., London*, (Series A) 396 425 (1984).

14. N.J. Carr and A.K. Galwey, Proc. Royal Soc., London, (Series A) 404 101 (1986).

15. A.K. Galwey and G.M. Laverty, Proc. Royal Soc., London, (Series A) 440 77 (1993).

16. M. Kony, Materials Research Laboratory, unpublished work (1991).

17. C. D. Hutchison, V. Krishna Mohan and R.W. Millar, Propellants, Explosives and Pyrotechnics, 9 161 (1984).