Thermochimica Acta, 148 (1989) 521-531
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

THERMAL ANALYSIS OF ENERGETIC MATERIALS

M.E. BROWN
Chemistry Department, Rhodes University, Grahamstown, 6140 South Africa

ABSTRACT

Substances which undergo strongly exothermic chemical reactions may constitute hazards in various situations. The techniques of thermal analysis, in general, and differential scanning calorimetry (DSC) in particular, provide ways of examining such substances, in small quanitities under relatively safe conditions. A brief review of some developments in thermal explosion theory relevant to thermoanalytical studies is given. Extrapolation of the results obtained from thermoanalytical tests to more realistic situations has to be done with great care. The findings of some recent studies on energetic materials are reviewed.

INTRODUCTION

Strongly exothermic chemical reactions may arise from intermolecular redox processes in pure or relatively pure compounds, e.g. many high-explosive compounds, or from interactions between oxidising and reducing constituents of mixtures, e.g. black powder and other pyrotechnic compositions, and propellants.

Once the exothermic reaction has started, depending upon the thermal contact with the surroundings, "thermal runaway" may occur, leading to explosion. The theory of thermal explosions in condensed phases has a vast literature (1,2), marked by many outstanding contributions from Gray, Boddington and colleagues (3-13).

Where the exothermic process takes place in the solid state, e.g. decomposition of metal azides and fulminates, allowance also has to be made for the influence of the "previous history" of the sample on its thermal stability. The way in which the sample has been crystallised, its impurity and defect content, and any mechanical treatment, such as grinding or

---

Thermal Analysis Highlights, 9th ICTA, Jerusalem, Israel, 21-25 August 1988.

pressing, can all influence its behaviour (14).

THERMAL RUNAWAY

For "thermal runaway" to occur, the rate of heat-generation by the reaction must be greater than the rate of heat-loss to the surroundings. Allowance may also have to be made for depletion of reactant (9). The rate at which heat is being produced by reaction, assuming that there is no change of mechanism during reaction (15), is

$$dq/dt = Q\ (d\alpha/dt) = kQ\ f(\alpha)$$

where Q = heat of reaction, α = fractional amount of reaction ($\alpha = 0$ at start and 1 at end of reaction). $f(\alpha)$ is some function of α and is often taken to be of the form $(1 - \alpha)^n$ and, often, n is taken as 1 (first-order). These assumptions are not good for exothermic processes (15) since they imply that reaction starts at maximum rate and that the rate then decreases (5). So-called autocatalytic behaviour is much more probable, once reaction has started by some other mechanism, with

$$f(\alpha) = \alpha^p(1 - \alpha)^q$$

usually with $p = q = 1$. This sort of behaviour can result (15) from: (i) chemical autocatalysis where the increasing presence of a reaction product increases the rate of reaction; (ii) depletion of a stabilizer; (iii) melting accompanying decomposition; or (iv) nucleation and growth in a solid-state reaction.

Generally the Arrhenius equation is assumed to apply to the temperature dependence of the reaction rate so that

$$dq/dt = Q\ f(\alpha)\ A\ \exp(-E/RT)$$

where E is the activation energy, and A the pre-exponential factor.

For a reaction of known kinetic mechanism and kinetic parameters, E and A, and known Q, the hazardous nature of the reaction will then depend upon the actual experimental conditions, especially the heat capacity and heat transfer conditions of the surroundings in relation to the sample size.

The equations for the rate of heat loss from the system depend on the model adopted for the system. One limiting situation is that of a uniform temperature throughout, with heat transfer taking place at a sharp boundary and a fixed ambient temperature, T_a (convective heat loss or Semenov (2) model). The other limit, which is more realistic for reactions in condensed phases, involves a continuous temperature gradient from the centre of the system to the boundary which is at the ambient temperature (conductive heat loss or Frank-Kamenetskii (1) model).

The Frank-Kamenetskii model (1), which also ignores reactant consumption, leads to a relationship where if the value of a dimensionless parameter, δ, exceeds a critical value, δ_{cr}, ignition or explosion of the sample will occur. The relationship is

$$\delta = a^2 \; Q \; E \; A \; (c_o)^n \exp(-E/RT_a)/(\lambda \; R \; (T_a)^2)$$

where E, A, R, and Q have been defined, a is a dimension of the sample (the radius if the sample is, or approximates to, a sphere; or the half-thickness of a slab of infinite cross-section), λ is the thermal conductivity of the sample, and c_o is the initial concentration of reactant involved in a reaction of order n. The value of δ_{cr} depends strongly on the shape of the sample and is 0.88 for infinite slabs, 2.00 for infinite cylinders and 3.32 for spheres. This relationship holds as long as E is not very small or T_a is not very large, i.e. the factor $\epsilon = RT_a/E$ must be less than about 0.25. Rogers (16) has done extensive experimental tests on such predictions, using samples of explosives of known size and shape. He points out that Q in the Frank-Kamenetskii equation should be the heat evolved during the self-heating process and is not the heat of combustion or of detonation.

The simpler theory above, has been extended to allow for additional factors such as reactant consumption (6), alternatives to the Arrhenius equation for expressing the temperature dependence of reaction rate (7), different combinations of thermal resistances (7), the temperature dependence of heat-transfer coefficients (8), the effect of a programmed increase of the ambient temperature (9), and the occurrence of simultaneous parallel reactions (10).

Allowance for reactant consumption (6) increases the value of δ_{cr} above its critical value δ_o when reaction consumption is ignored. The system least sensitive to reactant consumption is a spherical sample with significant diffusion and with distributed temperatures. Diffusion is thus fast enough to permit replenishment of the reactant consumed, giving an effectively constant reactant concentration. The other extreme is diffusion that is slow enough to be ignored. The relationship between δ_{cr} and δ_o is

$$\delta_{cr}/\delta_o = 1 + \Phi \; (g_w/B)^{2/3}$$

where Φ is a coefficient dependent upon geometry, g_w is an effective reaction order and B is a dimensionless adiabatic temperature rise (= c_o Q $E/\rho C \; R(T_a)^2$, where ρ is the density and C is the specific heat capacity of the reactant mixture.)

In dealing with the temperature dependence of reaction rate (7), the reduced-temperature, $\theta = (T - T_a)/(R(T_a)^2/E)$ and $\epsilon = (RT_a/E)$ are useful. The Arrhenius temperature dependence, $k = A \exp(-E/RT) = (A \exp(-E/RT_a))f(\theta)$ where $f(\theta) = \exp(\theta/(1 + \epsilon\theta))$. Frank-Kamenetskii used the approximation $f(\theta) = \exp(\theta)$ which requires small values of ϵ, while Boddington et al (7) have also used the "bimolecular" temperature dependence, $k = A'T^{1/2} \exp(-E/RT)$. With other factors being equal, δ_{cr} values are generally lower for systems following the "bimolecular" equation (7).

The thermal resistance of the system (7) is indicated by the Biot number, $Bi = \chi a/\lambda$, where χ is the surface heat transfer coefficient. The Semenov extreme corresponds to $Bi = 0$, and the Frank-Kamenetskii extreme to $Bi \rightarrow \infty$. Values of δ_{cr} at intermediate situations where both internal and boundary thermal resistances are important have been calculated (7).

When an exothermic reaction system is heated at a programmed temperature, the opposing effects of reactant consumption and heating of the reactant boundary may cancel each other (9). Under these conditions. the simple model of no external heating and negligible reactant consumption is a good approximation.

Where the exothermic system involves simultaneous parallel reactions (10), the definition of E is modified to a "communal" value based on the rate of energy release per unit volume by the whole system. The value to be used for δ is then the sum of the separate values of δ for the constituent reactions.

The features of actual temperature-time profiles when δ slightly exceeds its critical value have been examined (11). The temperature first increases rapidly and then changes very slowly for a long while before a final, rapid acceleration leads to ignition or explosion. The shapes of the profiles depend upon reactant geometry, the boundary conditions and the temperature dependence of reaction rate.

Thermal explosion theory has also been extended to deal with reactant particles dispersed in either an inert matrix (12) or a reactive matrix (13). The heat released by one particle influences the rate of heat-release from other particles. Additional parameters were introduced to compare the resistances to heat transfer of the reactant and the matrix material under various boundary conditions. Resistance to heat transfer may be concentrated at (i) the reactant/matrix interface, or (ii) at the matrix surface, or (iii) there may be some intermediate situation. As the thermal resistance of the matrix increases, the interaction between different reactant zones increases and the critical ambient temperature or the critical size may be decreased significantly. When the matrix material itself undergoes reaction, allowance has to be made for its rate of heat production. If the matrix decomposition is also exothermic, the heat of this additional reaction and the ratio of the activation energies for reaction in the matrix and in the reactant particles have to be taken into account. There is an optimum ratio of activation energies for which the system is most stable. If the matrix reaction is endothermic, the cooling effect will act counter to the lagging effect of the matrix on the reactant and the system may be stabilized. The alternative arrangement of endothermic reactant dispersed in a matrix of exothermic reactant material provides less stabilization. The shape of the embedded reactant zones is important but their distribution in the matrix and the matrix geometry are not.

Thermal sensitivity is obviously only one aspect of the total hazard evaluation of energetic materials. Treumann et al (17,18) have suggested a quantitative hazard number for explosives and pyrotechnic compositions based on the combined results of measurements of thermal stress, mechanical stress and detonation shock. Data for several ternary pyrotechnic systems have been presented in triangular diagrams (18).

To assess the thermal hazards of energetic materials, it is thus important to have as much information as possible on : (i) the thermochemistry of the reactions occurring; (ii) the kinetics and mechanisms of the reactions, and (iii) the thermophysical properties of each system and its surroundings.

Since the decompositions of energetic materials are nearly always complex processes, kinetic parameters can seldom, if ever, be related to a particular chemical step (15). Evaluation of thermal hazards must be based on the overall processes rather than on resolved stages. Information on the individual stages may provide insight into factors such as ageing and the effect of impurities.

Kinetic information, obtained at temperatures where rates of reaction are readily measurable, is often extrapolated using the Arrhenius equation, and assuming that the mechanism of reaction does not change with temperature, to predict the extent of reaction at storage temperatures, i.e. the effects of ageing, or to determine a safe-handling temperature. It is important to note that, according to the Arrhenius equation, the rate constant, k, for a reaction does not become zero even at very low temperatures. This assumes, of course, that the reaction mechanism does not change with temperature, and, for many explosives, the exothermic reaction takes place only once the material has melted. In such cases the material is usually safe at temperatures below the melting point. Thus any kinetic information obtained must not be extrapolated (15) to temperatures beyond the stability range of the observed phase.

THERMOANALYTICAL STUDIES

The techniques of thermal analysis, thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC), provide ways of determining the extent of reaction, α, and the thermochemistry of reaction, using small samples of potentially hazardous materials under relatively safe conditions. There have been several reviews of the use of thermal analysis in the examination of explosives (19,20) and of pyrotechnic compositions (21,22). Charsley et al (23) have studied the important role of binders in increasing the exothermicity of pyrotechnic compositions.

Widmann and Vogel (24) point out that DSC not only allows measurement of enthalpies of reaction, but also provides a valuable means of obtaining measurements of the heat capacities of the materials involved. Methods have also been proposed (25-27) for measuring thermal conductivities of materials, so that all this thermal information can be used to calculate the critical temperature for thermal runaway, or the maximum adiabatic temperature increase to be expected. This possible adiabatic temperature increase is a potential source of damage to thermal analysis instruments through, for example, the melting of aluminium sample pans. The occurrence of thermal runaway may give a characteristic "looped" trace in some DTA instruments as the sample temperature rises rapidly and then cools to the programmed temperature.

For mixtures, such as black powder (28), thermal analysis can provide information on the thermal behaviour of the individual constituents so that binary and even more complex interactions can be identified. It is particularly important to identify phase transitions and their temperatures as these often have an important bearing on the interactions. Simultaneous TG-DTA of black powder (28) showed that escape of sulphur from the mixture has to be prevented for the "pre-ignition" reaction between sulphur and molten KNO_3 to occur. The higher temperature oxidation of solid charcoal by molten KNO_3 then propagates the combustion of black powder. Sulphur forms extemely hazardous combinations with metal chlorates, and Storey (29) used DSC, DTA and hot-stage microscopy (HSM) to examine such combinations with from 1 to 30% sulphur. Sample self-heating, accompanied by lowering of the decomposition temperature, was greatest for high sulphur contents, large sample masses and slow heating rates. Reaction was detected at temperatures below the melting-point of S, but the heat evolved then melted the remaining S. Mixtures with S contents as low as 1% were classified as hazardous. Ficara and Moreira (30) have suggested a DSC method for the determination of elemental sulphur in mixtures from the areas of the melting endotherm.

ΔH values from DSC may be lower than values obtained from other techniques, such as bomb calorimetry, because of escape of volatile materials without ignition. Special high-pressure crucibles are available (24,31-35) for more volatile materials. Care has to be taken to exclude oxygen from such a system (24). Oxygen from the atmosphere may be essential for some interactions to occur.

In determining decomposition mechanisms, evolved gas analysis (EGA) is always valuable. Cronin and Brill (36), as part of a series of studies, used rapid-scan Fourier transform infrared spectroscopy to follow the gas evolution from decomposing energetic materials heated at rates up to 800°C s^{-1} and pressures up to 1000 psi, so that conditions were very similar to those during combustion. Detailed mechanisms could be derived and the occurrence of oscillating reactions was also observed (37).

The continuing controversy related to the use of isothermal or nonisothermal experiments for the determination of kinetic parameters obviously extends to this field. Nonisothermal methods require less time and less sample, but there are many reasons to believe (38)that isothermal measurements are likely to provide more reliable kinetic information.

The ASTM test (39) for characterizing hazardous materials is based on Ozawa's method (40) and involves measuring the temperature at the maximum of the exotherm, T_{max}, on DSC or DTG traces done at a series of different heating rates, β. The Arrhenius parameters can then be determined from a plot of ln (or log) β against $1/T_{max}$. Use of temperatures at the peak maximum or times to maximum rate may be misleading if there is an induction period to reaction. The activation energy (or temperature coefficient) of the process occurring during the induction period may differ considerably from that of the main reaction.

Rogers and Janney (15,16,41) have published extensively on the thermal analysis of hazardous materials. They recommend DSC measurements under isothermal conditions and give detailed procedures which include careful temperature calibration of the instrument used, and the avoidance of emittance errors caused by condensation of decomposition products on the sample holder. There is also a need to determine the effects of confinement pressure and volume on any kinetic parameters measured. They have made effective use of isotopic substitution in determining reaction mechanisms.

Nabiullah et al (42), faced with the problem of using explosives under high-temperature (hot hole) conditions, combined the information available from DSC and DTA with the results from some larger-scale simulations. Three types of explosives were examined: nitroglycerine (NG) based, a water-gel (slurry) and ammonium nitrate fuel oil (ANFO). The DSC traces for the NG-based explosives showed endotherms due to the phase transitions of ammonium nitrate (AN) and a large exotherm at 135°C corresponding to the decomposition of NG. Isothermal studies showed that the thermal stability decreased at temperatures greater than 100°C. An activation energy of 89.0 kJ mol^{-1} was calculated using a method similar to that of Ozawa, described above. Slurry explosives had slightly higher ignition temperatures (155 to 175°C) and ignition was preceded by the endothermic removal of water and the loss of gel-structure. The DSC traces for AN and ANFO were similar except that the fuel oil lowered the AN decomposition temperature. These observations were correlated with the behaviour of larger samples in simulated hot-hole conditions.

Rongzu et al (34) have applied their nonisothermal kinetic treatment (35) to the estimation from a single DSC curve of the activation energy, pre-exponential factor and reaction order for the exothermic decomposition of energetic materials in general (35) and for the 70% RDX/urea mixture in particular (34). In the latter paper (34), using the Semenov theory (2), they extended their calculations to estimation of a value of the critical temperature for thermal explosion. All the parameters calculated were interpreted as indicating the incompatibility and instability of the RDX/urea combination.

Tompa (43) used isothermal and programmed temperature DSC to determine the kinetic constants for thermal decomposition of a nitrate ester as used in a liquid monopropellant. Several different methods of kinetic analysis gave good agreement. Isothermal TG was found (43) to provide more useful information on the volatilization of nitroglycerine from a cross-linked double-base propellant than did dynamic TG. The rate of volatilization was found to be proportional to the thermal conductivity of the purge gas used, and, as might be expected, the greater the degree of cross-linking in the reactant, the slower the volatilization. Ageing, which destroys cross-linking, increased the rate of volatilization. Activation energies for volatilization varied somewhat with method of analysis, but were generally low (36 to 75 kJ mol^{-1}) and were attributed to a thermal transport mechanism, as supported by the atmosphere effect.

Some further recent thermoanalytical studies on the thermal stability of energetic materials include the use by Inoue et al (44) of sealed cell DTA to evaluate the fire and explosion hazards of various oxidants, through either their exothermic decompositions or reactions with combustible materials. Tables of temperatures of onset of reaction are given.

Minxiu and Hengyuan (45) have supplemented DSC studies with X-ray photoelectron spectroscopy (XPS) in examining the thermal stability of 2,4,6-trinitropyridine and its derivatives. Use of XPS enabled changes in the bonding situations of the different N atoms (46) to be determined.

Dilun and Haochuan (47) re-examined the decomposition of tetrazene, using DSC with sealed cells, and concluded that the rate of reaction is controlled by the diffusion of gaseous products. Molecular-orbital calculations suggested that the value of the activation energy obtained was close to that for the first electronic transition.

Studies (48) on bis(trinitroethyl-N-nitro)ethane (BTNE), using DSC, X-ray diffraction and scanning electron microscopy, showed that thermal stability was dependent upon the recrystallization procedure, which can introduce surface dislocations.

These examples show the value of complementary techniques in interpreting the results of thermoanalytical studies.

REFERENCES

1. D.A. Frank-Kamenetskii, "Diffusion and Heat Transfer in Chemical Kinetics", Plenum, New York, 2nd Edn., 1969, Ch. 7.
2. N.N. Semenov, "Some Problems of Chemical Kinetics and Reactivity", Vol. II, Princeton Univ. Press, 1959, Ch.VIII.
3. P. Gray and M.J. Harper, Proc. 4th Int. Symp. Reactivity of Solids, Elsevier, Amsterdam, (1960)283; Trans. Far. Soc., 55(1959)581.

4. P. Gray in C. Capellos and R.F. Walker (Eds), "Fast Reactions in Energetic Systems", D. Reidel, Dordrecht, (1981)171.
5. T. Boddington, P. Gray and S.K. Scott, Proc. Roy. Soc. Lond. A, 380(1982)29.
6. (a) T. Boddington, C-G. Feng and P. Gray, Proc. Roy. Soc. Lond. A, 391(1984)269.
   (b) A.R. Shouman and S. El-Sayed, Proc. Int. Symp. on Pyrotechnics and Explosives, China Academic Publishers, Beijing, (1987)665.
7. T. Boddington, C-G. Feng and P. Gray, Proc. Roy. Soc. Lond. A, 392(1984)301; 390(1982)247.
8. T. Bcddington, C-G. Feng and P. Gray, J. Chem. Soc., Faraday Trans. 2, 80(1984)1155; 79(1983)1481,1499.
9. T. Boddington, C-G. Feng, S.R. Kay and P. Gray, J. Chem. Soc., Faraday Trans. 2, 81(1985)1795.
10. T. Boddington, P. Gray and G.C. Wake, Proc. Roy. Soc. Lond. A, 393(1984)85.
11. T. Boddington, C-G. Feng and P. Gray, Proc. Roy. Soc. Lond. A, 385(1983)289.
12. T. Boddington, C-G. Feng and S.K. Scott, J. Chem. Soc., Faraday Trans. 2, 80(1984)973.
13. S.K. Scott, J. Chem. Soc., Faraday Trans. 2, 80(1984)1555.
14. H.D. Fair and R.F. Walker (Eds),"Energetic Materials", Vol.1, Plenum, New York,1977.
15. R.N. Rogers and J.L. Janney, Proc. 11th NATAS Conf., (1981)643,651.
16. R.N. Rogers, Thermochim. Acta, 11(1975)131.
17. H. Treumann, 7th Int. Pyrotech. Sem., IIT Res. Inst., (1980)878.
18. H.Treumann, G. Kruger and N. Pfeil, 13th Int. Pyrotech. Sem., IIT Res. Inst., (1988)785.
19. D.J. Whelan, R.J. Spear and R.W. Read, Thermochim. Acta, 80(1984) 149.
20. L.W. Collins and L.D. Haws, Thermochim. Acta, 21(1977)1.
21. P.G. Laye and E.L. Charsley, Thermochim. Acta, 120(1987) 325.
22. A. Cottrell, T. Boddington and P.G. Laye, Proc. Int. Symp. on Pyrotechnics and Explosives, China Academic Publishers, Beijing, (1987)17.
23. T.T. Griffiths, E.L. Charsley and J.A. Hider, 13th Int. Pyrotech. Sem., IIT Res. Inst., (1988)393.
24. G. Widmann and K. Vogel, Proc. 9th ICTA, Thermochim. Acta, 134 (1988)451.

25. J. Chiu and P.G. Fair, Thermochim. Acta, 34(1979)267.

26. G. Hakvoort and L.L. van Reijen, Thermochim. Acta, 93(1985)317 ; 85(1985)319.

27. T. Boddington, P.G. Laye and J. Tipping, Comb. Flame, 50(1983)139.

28. M.E. Brown and R.A. Rugunanan, Proc. 9th ICTA, Thermochim. Acta, 134(1988)413.

29. P.D. Storey, 13th Int. Pyrotech. Sem., IIT Res. Inst., (1988)765.

30. M.L.G. Ficara and E. Moreira, Proc. 9th ICTA, Thermochim. Acta., 134 (1988)435.

31. W.D. Emmerich, E. Kaiserberger and H. Pfaffenberger, Proc. 11th NATAS Conf., (1981)625.

32. C.M. Earnest, R.L. Fyans and W. Kunze, Proc. 11th NATAS Conf., (1981)625.

33. P. le Parlouer, Proc. 11th NATAS Conf., (1981)625.

34. H. Rongzu, Y. Zhengquan and L. Yanjum, Proc. 9th ICTA., Thermochim. Acta, 134(1988)429.

35. H. Rongzu, Y. Zhengquan and L. Yanjum, Thermochim. Acta, 123(1988)135.

36. J.T. Cronin and T.B. Brill, Appl. Spectrosc., 41(1987)1147.

37. J.T. Cronin and T.B. Brill, J. Phys. Chem., 90(1986)178.

38. P.D. Garn, Proc. 9th ICTA, Thermochim. Acta, 135(1988)71.

39. R.B. Cassel, Perkin-Elmer Thermal Analysis Application Study, no. 28 (1979).

40. T. Ozawa, J. Thermal Anal., 2(1970)301.

41. R.N. Rogers and J.L. Janney, Proc. 7th ICTA, Vol II, Wiley, Chichester, (1982)1426,1434; Proc. 12th NATAS Conf., (1983)469,474.

42. MD. Nabiullah, R.N. Gupta, B. Singh and P.K. Gandopadhyay, Proc. 9th ICTA, Thermochim. Acta, 134(1988)419.

43. A.S. Tompa, J. Hazardous Materials, 4(1980)95.

44. Y. Inoue, F. Yoshizawa and Y. Kaneko, Proc. Int. Symp. on Pyrotechnics and Explosives, China Academic Publishers, Beijing, (1987)763.

45. Z. Minxiu and L. Hengyuan, Proc. Int. Symp. on Pyrotechnics and Explosives, China Academic Publishers, Beijing, (1987)214.

46. W. Jianqui and L. Hengyuan, Proc. Int. Symp. on Pyrotechnics and Explosives, China Academic Publishers, Beijing, (1987)425.

47. S. Dilun and H. Haochuan, Proc. Int. Symp. on Pyrotechnics and Explosives, China Academic Publishers, Beijing, (1987)402.

48. S. Quancai and W. Wendi, Proc. Int. Symp. on Pyrotechnics and Explosives, China Academic Publishers, Beijing, (1987)407.