LA-UR-82-887

Conf-820809--3

LA-UR--82-887

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MASTER

TITLE: THERMOCHEMISTRY OF MIXED EXPLOSIVES

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SUBMITTED TO: 7th International Conference on Thermal Analysis, Ontario, Canada, August 1982

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THERMOCHEMISTRY OF MIXED EXPLOSIVES

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INTRODUCTION

In order to predict thermal hazards of high-energy materials, accurate kinetics constants must be determined [1]. Predictions of thermal hazards for mixtures of high-energy materials require measurements on the mixtures, because interactions among components are common.

A differential-scanning calorimeter (DSC) can be used to observe rate processes directly, and isothermal methods enable detection of mechanism changes [2,3]. Rate-controlling processes will change as components of a mixture are depleted [3,4], and the correct depletion function must be identified for each specific stage of a complex process.

A method for kinetics measurements on mixed explosives can be demonstrated with Composition B [5,6]. Comp B is an approximately 60/40 mixture of RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) and TNT (2,4,6-trinitrotoluene), and it is an important military explosive.

Kinetics results indicate that the major process is the decomposition of RDX in solution in TNT with a perturbation caused by interaction between the two components. The kinetics constants measured for the global decomposition process have provided an excellent predictive model for the thermal initiation of Comp B.

EXPERIMENTAL

Apparatus. All measurements were made with a Perkin-Elmer Model DSC-1B differential-scanning calorimeter. Samples were sealed in aluminum cells, Perkin-Elmer Part Number 219-0062, and the cells were perforated with a single hole approximately 0.15 mm in diameter.

Sample. Composition B, Grade A, was used. It has a nominal composition of 59.5% RDX, 39.5% TNT, and 1% wax, and it is produced according to military specification MIL-C-401C, dated 15 May 1968.

Procedure. Temperature accuracy is extemely important in kinetics measurements; therefore, both the average and differential temperatures of the DSC must be calibrated with care. Calibrations must be made as close as possible to the temperature of measurement. The differential-temperature calibration can be made and the cell support can be checked for quality by "emission balancing" [7].

Both sample and reference cells must be perforated to maintain constant pressure. Unperforated sealed cells bulge at higher temperatures, causing baseline discontinuities. Uniform holes are easily made by adjusting the conical angle of the tip of a needle and punching through the sample-cell cover and a sheet of plastic that is 0.05-0.10-mm thick. The effect of lid perforation on apparent rate constant can be observed by making replicate runs at the same temperature with different numbers of holes of different sizes. If significant sample is lost by volatilization, the apparent rate constant will be seen to increase with hole size. The sample must not be allowed to spatter or boil out, as significant emittance changes will be made by contamination on the outside of the cell.

Mixtures present a sampling problem. Since samples of only 1 to 5 mg are usually used, extreme care must be taken to ensure as much homogeneity as possible without altering the sample.

After calibration with the appropriate temperature standard, the DSC is set at the desired test temperature, and the differential temperature control is adjusted again by emission balancing. The empty cell is removed from the sample support, the desired range is selected, the recorder is started (and the automatic data acquisition system, if one is used), and the sample is dropped quickly onto the sample support. A sharp break will appear on the record as the sample touches the support, but thermal equilibrium will normally be reestablished within one minute. If the recorder pen does not reappear within 75 s, an endothermic process is probably involved. If the pen recovers quickly but no additional signal is obtained, either the reaction was completed during the warmup time or a very

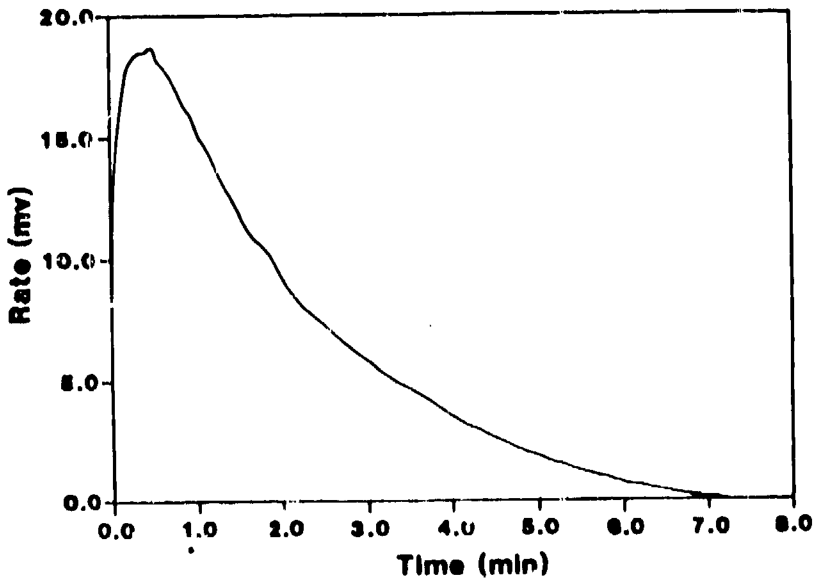

Figure 1. Isothermal DSC rate curve for Comp B at 500 K, normalized to 1 mg, range 1.

long induction time is involved. This can be determined by opening the cell and observing the condition of the sample. When isothermal runs of high-energy materials are made within a suitable temperature range, rate curves similar to Figure 1 will be obtained. Each run should be allowed to continue long enough to identify the infinite time baseline. When automatic data-acquisition and processing equipment are not available, rate curves can be evaluated with a ruler by extending the infinite-time baseline back to zero time and measuring the deflection from this baseline at as many equally spaced times as are practicable. The rate curve can be integrated by using Simpson's Rule, and the fraction reacted at any time, α, is obtained by dividing the fractional area to that time by the total area. These simple measurements of the deflection above the infinite-time baseline, the fraction reacted, and time are the only input data required for all further calculations.

As the first step in the evaluation of the kinetics data obtained from mixtures of high-energy materials, it is necessary to determine whether there is a significant interaction among the components during the primary self-heating reaction The simplest observation of complexity and/or measurement of reaction order and reaction stoichiometry can be obtained from an "order plot" [4,8]. It is dangerous to use kinetics evaluations made from assumed rate laws to make thermal-hazards predictions for high energy materials. The correct reaction order function, or, in the case of complex reactions, the correct depletion function must be used for the evaluation of rate data. We strongly recommend that order plots be produced early in the evaluation of any rate data.

An order plot is a graph of the log of the deflection (in any consistent units) versus the log of the residual fraction $(1 - \alpha)$. The reaction order for a specific extent of reaction is shown by the slope of a straight line. Negative slopes and curved lines indicate complex processes such as melting with decomposition, autocatalysis, and solid-state reactions. When complexity is observed, autocatalytic or nucleation-growth-type functions can often be used for data evaluation [2,3,9].

RESULTS AND DISCUSSION

An order plot for the decomposition of Comp B is shown in Figure 2. The order of the global reaction is exactly 1.0, so Comp B rate data can be evaluated according to a first-order rate law, $d\alpha/dt = k(1 - \alpha)$. Rate constants can be determined very simply from the isothermal DSC data [10]. Relative recorder deflections, b, and time, t, are the only data required, as follows:

$$\ln b = C - kt, \qquad (1)$$

where k is the rate constant (s^{-1}), and C is a constant.

A total of 16 independent rate measurements were made with Comp B over a temperature range of 30 K (from 495 to 525 K). The resulting Arrhenius plot (Figure 3) is linear, and it gives an activation energy (slope = -E/R, where R is the gas constant) of 180.2 kJ mole^{-1} and a pre-exponential (intercept) of 4.62 X 10^{16} s^{-1}.

Pure RDX gives first-order kinetics constants through much of its decomposition in the pure liquid phase, with E = 197.1 kJ mole^{-1} and Z = 2.02 X 10^{18} s^{-1}. We believe that the currently "best" kinetics constants for pure TNT are E = 143.9 kJ mole^{-1} and Z = 2.51 X 10^{11} s^{-1} [1]. It must be emphasized that these kinetics constants apply primarily to predictions of critical temperatures: they are not intended to be used for all predictive models. A simple comparison of activation energies is not especially informative with regard to hazard analysis.

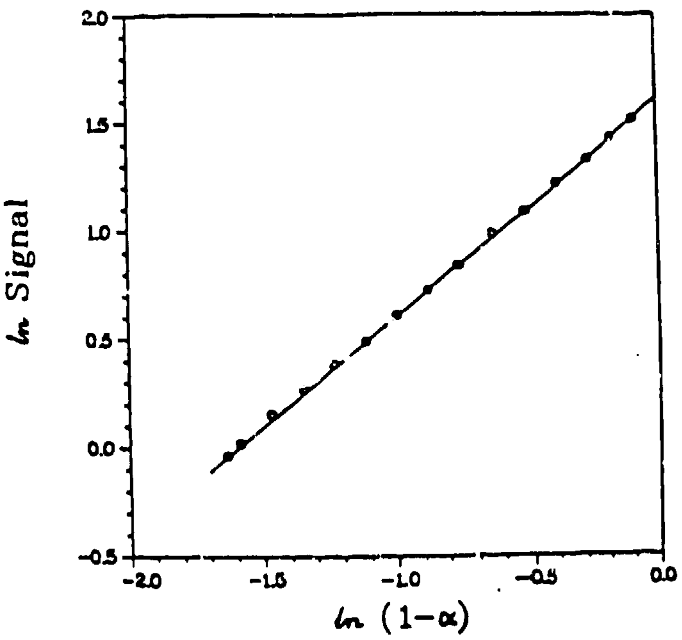

Figure 2. Order plot for the decomposition of Comp B. The segment shown was calculated from the part of the rate curve that showed a positive order.

The most important fact to establish with regard to thermal hazards is whether a high-energy material will self heat catastrophically. Consequently, we use the kinetics constants determined for any system to produce a predictive model for the critical temperature, T_c, of that system. The critical temperature is defined as the lowest constant surface temperature at which catastrophic self heating can occur in a high-energy material of a specific size and shape. A predictive model for critical temperature can often be obtained from the following expression [11]:

$$\frac{E}{T_c} = R \ln\left[\frac{a^2 \rho Q Z E}{T_c^2 \lambda \delta R}\right] , \qquad (2)$$

where R is the gas constant (8.314 J mole^{-1} K^{-1}), a is the radius of a sphere or cylinder or the half-thickness of a slab, ρ is the density, Q is the heat of reaction during the self-heating process (not expected to be the same as the heat of detonation or combustion), Z is the pre-exponential and E the activation energy from the Arrhenius expression, λ is the thermal conductivity, and δ is a shape factor (0.88 for infinite slabs, 2.00 for infinite cylinder and 3.32 for spheres). E and Z are the largest numbers in the equation, and their accuracy determines the accuracy of the predictions made from the model.

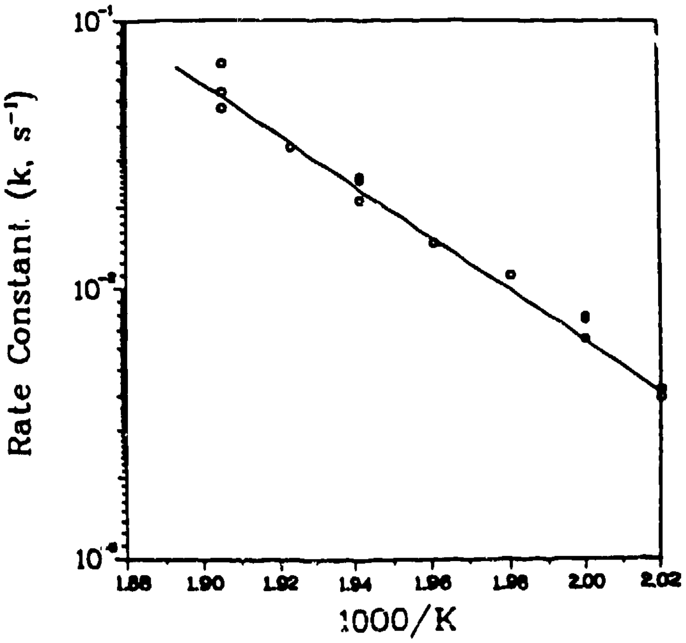

Figure 3. Arrhenius plot for Comp B.

We strongly believe that it is dangerous to rely on predictive models based only on chemical kinetics determinations, because of several types of errors that may occur without being detected. The most probable cause of error is that the values of E and Z may be based on the wrong part of the decomposition reaction. Identification of the mechanism that leads to catastrophic self-heating is particularly difficult with complex materials and mixtures. Also, errors can be made in the thermal conductivity measurement, and the Frank-Kamenetskii equation may not provide an accurate model for low-energy systems. Heat-of-reaction values may also be in error.

The heat of reaction for the decomposition of a material may be observed to vary with pressure and/or confinement, and high-energy materials differ in their responses to pressure and confinement. Therefore, it is important to test predictive models under different confinement than used for kinetics measurements. A system sensitive to confinement will be detected by a lack of agreement between the predicted T_c and the experimental T_c, but a lack of agreement does not always indicate a system sensitive to confinement. If a lack of agreement is observed, a "fail-safe" (but often unrealistic) predictive model may be produced by using the maximum possible heat of reaction (for example, the heat of detonation) for the system. The largest heat of reaction for Comp B that could be measured under any experimental conditions with the DSC was 2.85 kJ g^{-1}.

Because of the difficulties with measurements of kinetics constants, thermal conductivity, and heat of reaction, we strongly recommend independent methods for testing the accuracy of T_c predictions [1,12]. We do this on a laboratory scale with a time-to-explosion test. This involves weighing samples into aluminum blasting caps, confining them, measuring their thicknesses, and immersing them in a liquid metal bath at a known temperature. Times to explosion are measured for different temperatures, and the lowest temperature at which the sample will explode is the critical temperature for that size and shape.

Our experimental determination of T_c [1] was run with a measured average sample thickness of 0.795 mm for a 40 mg sample at a calculated density of 1.577 g cm^{-3} (91% TMD). Times to explosion were measured as a function of temperature until the lowest

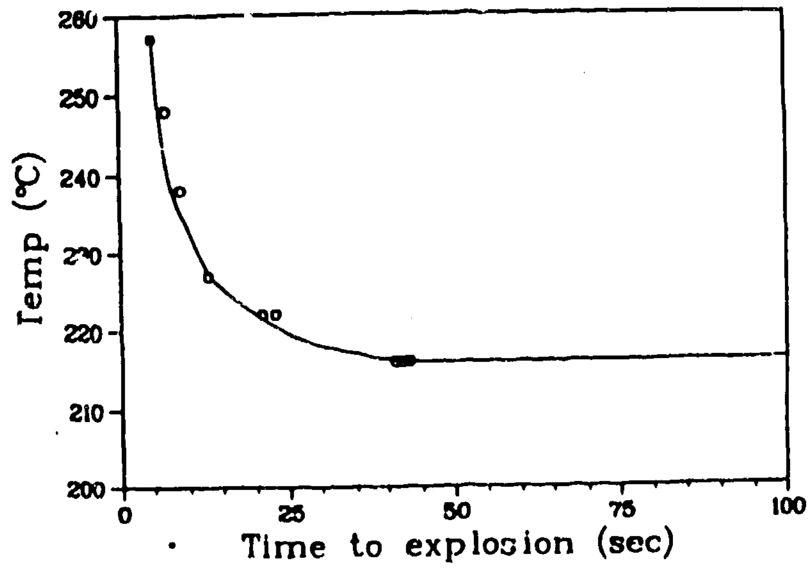

Figure 4. Time-to-explosion plot for 40-mg confined samples of Comp B.

temperature giving an explosion was identified, as shown in Figure 4. The experimental T_c for our particular size and shape was determined to be 489 K (216°C).

The predicted value for T_c with the size, shape, and density used in the experimental determination is 489 K. The values used in equation (2) were the following: $a = 0.040$ cm, $\rho = 1.577$ g cm^{-3}, $Q = 2.85$ kJ g^{-1}, $Z = 4.62 \times 10^{16}$ s^{-1}, $E = 180.2$ kJ mole^{-1}, $\lambda = 1.98 \times 10^{-3}$ J cm^{-1} s^{-1} K^{-1}, and $\delta = 0.88$ (for a slab). The perfect check between the experimental and predicted values is unusual, but we normally hope to obtain agreement within ±5 degrees.

CONCLUSIONS

A combination of chemical kinetics and experimental self-heating procedures provides a good approach to the production of predictive models for thermal hazards of high-energy materials. Systems involving more than one energy-contributing component can be studied. Invalid and dangerous predictive models can be detected by a failure of agreement between prediction and experiment at a specific size, shape, and density.

Rates of thermal decomposition for Composition B appear to be modeled adequately for critical-temperature predictions with the following kinetics constants: $E = 180.2$ kJ mole^{-1} and $Z = 4.62 \times 10^{16}$ s^{-1}.

REFERENCES

1. R.N. Rogers, Thermochimica Acta, 1975, 11, 131.
2. R.N. Rogers and J.L. Janney, Proceedings of the Eleventh North American Thermal Analysis Society Conference, Vol. II, John P. Schelz, Editor, Johnson & Johnson Products, Inc., New Brunswick, NJ, 1981, 643.
3. J.L. Janney and R.N. Rogers, ibid, 651.
4. R.N. Rogers, Fraunhofer-Institut für Trei- bund Explosivstoffe, International Meeting, "Testing Methods for Propellants and Explosives," Karlsruhe, Germany, 1980, 59.
5. T.R. Gibbs and A. Popolato, "LASL Explosive Property Data," University of California Press, Berkeley, (1980), p.11.
6. AMCP 706-177, "Explosives Series, Properties of Explosives of Military Interest," 1971, 46. Foreign requests for this document must be submitted through the Washington, D.C., embassy to: Assistant Chief of Staff for Intelligence, Foreign Liaison Office, Department of the Army, Washington, D.C. 20310, USA.
7. L.W. Ortiz and R.N. Rogers, Thermochimica Acta, 1972, 3, 383.
8. R.N. Rogers, Thermochimica Acta, 1972, 3, 437.
9. T.B. Tang and M.M. Chaudhri, J. Thermal Anal., 1979, 17, 359.
10. R.N. Rogers, Anal. Chem., 1972, 44, 1336.
11. D.A. Frank-Kamenetskii, Acta Physicochem. URSS, 1939, 10, 365.
12. D.L. Jaeger, LA-8332, University of California, Los Alamos Scientific Laboratory, Box 1663, Los Alamos, NM 87545, USA, 1980.

The work reported was performed with support from the U. S. Army Armament Research and Development Command, Dover, N.J., Joseph Hershkowitz, Program Manager.