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LASL METHODS OF DERIVING MODELS FOR PREDICTING THE THERMAL HAZARDS AND USEFUL LIFETIMES OF EXPLOSIVES

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Sensitivity, thermal stability, and toxicity are the three major safety factors that must be considered in selecting an explosive for any specific application. At the Los Alamos Scientific Laboratory (LASL) we attempt to obtain quantitative data on these factors at the earliest possible stage in the development of any new explosives system. This paper will consider only the problems associated with thermal stability; some aspects of the LASL philosophy concerning sensitivity will be discussed by L. C. Smith.

Our first goal in studying the thermal stability of explosives was to provide models for predicting thermal hazards. It was desired to be able to sample the first small-scale preparation of a new explosive, make an accurate determination of the kinetics constants for its decomposition, and predict safe handling conditions for fabrication and application. It was presumed that the kinetics methods could also be used to derive lifetime predictive models for systems in which chemical reactions are responsible for the critical degradation processes. We believe that we have been largely successful in attaining our first goal, and we have successfully predicted some long-term degradation rates from small-scale measurements.

When one is attempting to derive a practical, reliable predictive model for the self-heating of an explosive, I consider it imperative that the kinetics measurements be based on heat-evolution rates. Therefore, our preferred method for the determination of kinetics constants uses isothermal differential calorimetry[1-4]. The heat-evolution rates of milligram-size samples are observed with a Perkin-elmer Differential Scanning Calorimeter operated at a series of constant temperatures. Rate constants are obtained from the slopes of plots of signal amplitude versus time, and operational activation energies and pre-exponentials are obtained from Arrhenius plots of the rate-constant data. "Order plots"[2] of the rate data give direct measurements of reaction orders, reveal any complexities, and enable determination of the stoichiometry in mixed systems.

In predicting the thermal safety of any specific size and shape of explosive charge, the critical temperature (T_m) is defined as the lowest constant surface temperature above which a thermal explosion can result from the self-heating of the explosive. The heat-balance problem involved in the prediction of T_m has been considered[5-7], and the following simple expression allows predictions to be made that are of adequate accuracy for most research and development purposes:

$$\frac{E}{T_m} = R \ln\left[\frac{a^2 \rho Q Z E}{T_m^2 \lambda \delta R}\right] .$$

E is the activation energy of the decomposition reaction, R is the gas constant, 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, Z is the pre-exponential, λ is the thermal conductivity, and δ is a shape factor (0.88 for infinite slabs, 2.00 for infinite cylinders, 2.72 for a regular right-circular cylinder, and 3.32 for a sphere).

It is obvious from the expression for the prediction of the critical temperature that there is no such thing as a single "autoignition temperature" for an explosive. The temperature at which an explosive can self-heat to explosion will depend very critically on size and shape. Small-scale autoignition tests will give high values for critical temperatures, and explosive devices designed on the basis of such determinations can be dangerous.

Autoignition or time-to-explosion tests can be useful, however, if they can be used to produce an independent experimental value for the critical temperature of any explosive composition. This independent experimental value can be used to test the predictive model derived from kinetics measurements. It is important to recognize, however, that the physical values required for the predictive expression (for example, density, thickness, and shape) must be known for the critical-temperature test assembly.

For practical purposes, the experimental method for the determination of critical temperatures should be adaptable to laboratory operations. It must, therefore, be a compromise between accuracy of definition of conditions and violence of reaction. The method in use at LASL[8] was designed to be as inexpensive as possible and to be used as a routine survey method. It is used to test predictive models, as a control test for explosive quality, and to detect incompatible systems. We have shown that calculated and experimental critical temperatures agree very well[8], allowing predictions for larger systems to be made with some confidence on the basis of small-scale tests. Complex systems that do not allow successful predictions to be made can be detected with small samples, and suitable care can be exercised in further testing.

Some organic explosives decompose at significant rates only in the homogeneous liquid phase (for example, TNT and TNB), a very few appear to decompose completely in the solid state (the most common being TATB), but most melt with decomposition (for example, RDX, HMX, PETN, and HNS). When the critical temperature of an explosive is below its nominal melting point, it must decompose in the solid state, usually a slow process, until some change allows its decomposition rate to increase sufficiently for it to self-heat to explosion. The critical temperature will be determined by the process showing the maximum rate attainable in a condensed-phase reaction for the explosive in question, but the time to explosion may be largely determined by the low-rate, solid-state reactions. This is an important distinction, because we can usually measure the kinetics constants for the most rapid reaction quite accurately, and, consequently, we can predict critical temperature with some confidence. However, the solid-state reactions involved in time-to-explosion estimations are difficult to measure accurately, and the solid-state rates can vary tremendously with changes in purity and crystal perfection. Attempts to compare systems by use of time-to-explosion tests alone can be misleading.

I believe that the thermal safety of pure explosives and explosive compositions can now be specified with some confidence on an absolute basis. There is no need to standardize relative tests. When the values required for application of the critical temperature expression have been obtained and the accuracy of the derived predictive model for any system has been successfully demonstrated by use of an independent experimental method, objective comparisons among explosives and compositions can be made, safe fabrication conditions can be selected, and the safety of device deployment under different conditions can be predicted.

Safety studies on explosives should consider time-dependent changes in sensitivity, stability, and toxicity. A change in any one of the safety factors that renders a device useless can provide a "critical-lifetime criterion" for the device; however, it should be recognized that many processes other than chemical reactions can cause ultimate failure of a system to function properly or to become too dangerous to use.

When degradation or changes in thermal hazard provide the critical-lifetime criterion, predictive models for lifetime may be derived from thermochemical methods; however, certain precautions must be observed. Predictive models based on solid-state decomposition rates may be unreliable for the same reasons that time-to-explosion calculations are unreliable, heterogeneous reactions may be overlooked as the result of different loading densities in experimental systems compared with production devices, and mechanism changes are likely between service temperatures and thermal test temperatures. Mechanism changes are almost certain when there are phase changes between service temperatures and test temperatures.

I do not believe that a standard procedure can be proposed for the derivation of lifetime predictive models; however, I do believe that standard thermal tests should be used to detect thermal hazards that appear as the result of aging of the explosive or device.

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