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CHEMICAL-DECOMPOSITION MODELS FOR THE THERMAL EXPLOSION OF CONFINED HMX, TATB, RDX, AND TNT EXPLOSIVES*

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Chemical decomposition models have been deduced from the available chemical kinetic data on the thermal decomposition of HMX, TATB, RDX, and TNT. A thermal conduction model is used in which the thermal conductivity of the reacting explosive decreases linearly with the mass fraction reacted to that of the gaseous products. These reactive heat flow models are used to predict the time to explosion versus reciprocal temperature curves from several heavily confined explosive tests. Good agreement is obtained between experimental and calculated explosion times for the pure explosives HMX, TATB, RDX, and TNT, mixtures such as RX-26-AF (HMX/TATB), Octol (HMX/TNT), and Comp B (RDX/TNT), and for PBX 9404, an HMX-based explosive containing an energetic nitrocellulose binder.

INTRODUCTION

The heavily confined One-Dimensional Time to Explosion (ODTX) experimental apparatus was developed as a well-controlled environment in which to measure times to explosion at confinement pressures up to 1500 atm. Such an environment is amenable to computer modeling by a heat transfer code containing the appropriate chemical kinetic energy source terms. The ODTX apparatus and the initial experimental and modeling results were discussed by Catalano et al.,[1] who demonstrated the effects on time to explosion of the applied closing and holding pressures. That paper also showed that the time to explosion could not be accurately calculated by a single Arrhenius chemical kinetic energy release term or by a two reaction sequence model in which the first reaction is the endothermic formation of a reactive intermediate. The experimental effects of geometry and void volume on the time to explosion in the ODTX apparatus were investigated by Tarver et al.,[2] who also demonstrated that with an appropriate description of the principal energetic rate processes and a knowledge of the thermal diffusion of the

explosive as a function of temperature, the time to explosion versus reciprocal temperature curves HMX, TATB, and TNT could be accurately calculated. More information has since been generated by various researchers on the reactions involved in the chemical decomposition process and on their kinetic parameters. ODTX data has been obtained on more explosive molecules and mixtures of explosives. Other well-defined thermal explosion tests have also been developed. Therefore, in this paper, chemical decomposition models for four explosives (HMX, RDX, TATB, and TNT) are presented and used to calculate time to explosion versus reciprocal temperature curves from several confined experiments for these four explosives and three mixtures, RX-26-AF (HMX/TATB), Octol (HMX/TNT), and Comp B (RDX/TNT). The effect of an energetic binder on the time to explosion in the ODTX test is examined for the HMX-based explosive, PBX 9404, which contains an energetic nitrocellulose binder.

CHEMICAL DECOMPOSITION MODELS

A. HMX and RDX

The chemical reactions involved in the thermal decomposition processes of HMX and RDX have been investigated by many techniques, and several possible sequences have been proposed.[3-6] While these sequences contain different postulated radical reactions, all of the

available data suggests that the energy deposition and uptake can be described by three relatively slow processes that control the time to explosion. The first step is the endothermic breaking of C-N bonds in the ring forming $H_2C=N-NO_2$ and the other ring fragments that have frequently been observed in mass spectrometric studies, i.e., a depolymerization of the RDX or HMX rings.[3] This reaction appears to be the slowest step in the decomposition process and to have an activation energy of approximately 52 kcal/m for HMX and 47 kcal/m for RDX, as measured by Robertson[7] and Rogers.[8] The second major step is the slightly exothermic rearrangement of $H_2C=N-NO_2$ into either CH_2O and N_2O or HCN and HNO_2, which leads to $\cdot NO_2$ radicals. Both sets of products have been observed under different conditions, but identification of the dominant process is complicated by the rapid reaction of formaldehyde with $\cdot NO_2$ radicals. For our modeling purposes, the second step is assumed to be the decomposition of $H_2C=N-NO_2$ into two gaseous molecules with an activation energy of approximately 44 kcal/m, as measured in several mass spectrometric studies.[3] The third major step is the very exothermic gas phase decomposition of CH_2O+N_2O (and/or $HCN+HNO_2$) into the stable gaseous products H_2O, N_2, CO, CO_2, etc. Flanagan[9] has determined the kinetics of the gas phase reaction of CH_2O+N_2O, and the kinetics of most of the other possible gas phase reactions have been measured. An overall activation energy for these gas phase reactions of 34 kcal/m is used for the third and final step in this decomposition model. We postulate an essentially identical model for RDX as HMX except for the first step which shows the effect of the lower crystal energy and smaller ring. Thus the HMX and RDX decomposition model is

$$A \xrightarrow{1} B \xrightarrow{2} 2C \xrightarrow{3} D \qquad (1)$$
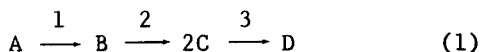
where A represents HMX or RDX, B represents $H_2C=N-NO_2$, C represents (CH_2O+N_2O) or $(HCN+HNO_2)$, and D represents the final products. Table I lists the heat of reaction and kinetic parameters for each reaction.

This 3 reaction, 4 species model is incorporated into the TACO heat transfer code,[10] which can be modified to include any number of chemical reactions and species. For this model the heat flow equation to be solved is where λ is the thermal conductivity,

$$-\lambda \nabla^2 T + \rho C \frac{\partial T}{\partial t} = N_A q_1 Z_1 e^{-E_1/RT}$$
$$+ N_B q_2 Z_2 e^{-E_2/RT} + N_C^2 q_3 Z_3 e^{-E_3/RT} \qquad (2)$$

∇ is the LaPlacian operator, T is temperature in K, ρ is density, C is heat capacity, $N_{A,B,C,D}$ are the respective mole fractions such that $N_A + N_B + N_C + N_D = 1$ from Eq. (1), q is heat of reaction, Z is the frequency factor, E is activation energy, R is the gas constant, and the subscripts refer to reactions 1, 2, and 3 in Eq. (1).

B. TNT

As reviewed by Guidry et al.,[11] the kinetic studies of TNT decomposition have indicated that this process is an autocatalytic one in which a reactive immediate is formed which subsequently reacts with TNT molecules to produce gaseous reaction products. Therefore TNT is modeled as an autocatalytic three reaction process

$$A \xrightarrow{1} B$$
$$A+B \xrightarrow{2} C \qquad (3)$$
$$B+B \xrightarrow{3} C$$

where A represents TNT, B represents the reactive immediate, and C represents the final products. Guidry et al.[11] showed that the reported kinetic measurements fall into two catagories: those which measure the rate of the endothermic, "induction" process of reaction,(1) which has an activation energy of approximately 44 kcal/m, and those which yield a rate for the exothermic process (reactions (2) and/or (3)) of approximately 34 kcal/m. The actual values used for TNT are listed in Table I. The resulting heat flow equation is

$$-\lambda \nabla^2 T + \rho C \frac{\partial T}{\partial t} = N_A q_1 Z_1 e^{-E_1 RT}$$
$$+ N_A N_B q_2 Z_2 e^{-E_2/RT} + N_B^2 q_3 Z_3 e^{-E_3/RT} \qquad (4)$$

C. TATB

Less is know about the thermal decomposition of TATB than the previous three explosives. Farber and Srivastava[12] studied the sublimation and the early time endothermic bond breaking process in TATB. Workers at Los Alamos National Laboratory and Lawrence Livermore National Laboratory have shown that a considerable amount of water can be driven out of TATB before it reacts exothermically.[13,14] The kinetics of the exothermic process measured by Rogers[8] and Bailey[15] indicate that its activation energy is approximately 60 kcal/m. Based on this data, TATB is assumed to undergo an autocatalytic process similar to Eq. (3) for TNT, except that the activation energy for the endothermic first step is less than those for the exothermic second and third steps. Therefore a considerable amount of the solid reactive immediate (or immediates), which has not yet been positively identified, should be produced before the exothermic process can dominate. Table I contains the parameters used for TATB and the heat flow equation is given by Eq. (4).

D. Nitrocellulose

As shown in the Results Section, the energetic binder in PBX 9404 which contains nitrocellulose influences the time to explosion, even although

PBX 9404 is 94% HMX, 3% tris-β-chloroethylphosphate and only 3% nitrocellulose. To model PBX 9404, the recent kinetic results for nitrocellulose obtained by Volltrauer and Fontijn[16] are used in a two-step, autocatalytic sequence

$$A \xrightarrow{\ 1\ } B$$
$$A+B \xrightarrow{\ 2\ } C \qquad\qquad (5)$$

in which the endothermic first reaction has a 39 kcal/m activation energy and the exothermic second reaction has a 26.3 kcal/m activation energy. In the PBX 9404 model, 6% of the explosive is assumed to be binder with these nitrocellulose kinetics and to have an overall heat of reaction of 600 cal/g. This is equal to approximately one-half of the nitrocellulose heat of reaction, since only one-half of the binder is nitrocellulose. Since 94% of the explosive is HMX, the thermal conductivity and heat capacity curves for HMX are used in the heat flow calculations.

It must be noted that the stabilizer in the nitrocellulose is not included in the calculation. Yet we have observed that its presense does effect the time to explosion. Thus these kinetic parameters are illustrative of a certain batch of nitrocellulose. The exothermic process is principally affected.

Table I.
Kinetic and thermal properties used in the heat flow calculations.

Explosive	HMX	TATB	RDX	TNT	Nitro-cellulose
q_1(cal/g)	-100	-50	-100	-30	-30
$\ln Z_1$	48.7	29.5	45.5	35.0	35.6
Ea_1(kcal/m)	52.7	42.0	47.1	44.0	39.0
q_2(cal/g)	300	900	300	900	630
$\ln Z_2$	37.5	45.0	40.7	26.0	32.0
Ea_2(kcal/m)	44.1	60.0	44.1	34.5	26.3
q_3(cal/g)	1200	950	1200	930	–
$\ln Z_3$	28.1	45.0	35.0	26.2	–
Ea_3(kcal/m)	34.1	54.0	34.1	33.5	–
C(cal/gK) at 20°C	0.24	0.26	0.24	0.27	–
C(cal/gK) at 350°C	0.42	0.43	0.42	0.40	–
λ(cal/cm-s-°C) at 20°C	1.23×10^{-3}	1.91×10^{-3}	6.22×10^{-4}	6.2×10^{-4}	–
λ(cal/cm-s-°C) at 160°C	9.70×10^{-4}	1.42×10^{-3}	4.85×10^{-4}	5.7×10^{-4}	–
Melting Point (°C)	–	–	204	81	–
Heat of Fusion (cal/g)	–	–	38.4	22.3	–

THERMAL CONDUCTION MODEL

Along with the chemical kinetic parameters, the thermal conductivity and heat capacity of the explosive as functions of temperature are important inputs to the time to explosion calculations. These thermal properties have been measured[17] for HMX and TATB up to 160°C and will soon be measured before and after melting for TNT and RDX by a technique recently developed for liquids.[18] In the previous calculations,[2] the thermal conductivities of the reacting explosives above 160°C were assumed to follow the extrapolated curves for the unreacted explosives. As shown in Fig. 6 of Tarver et al.,[2] the product gases have thermal conductivities an order of magnitude lower than HMX and TATB. In the present calculations, the thermal conductivity of the reacting explosive is assumed to decrease linearly to the gas phase value with the mass fraction that has been converted to gaseous products (N_C+N_D in the HMX/RDX model and N_C in the TNT/TATB model). This thermal conduction assumption yields an improved description of the heat flow both at high temperatures, where the outer layers of explosive are rapidly generating gaseous products, and at low temperatures, when the entire explosive is heated and is slowly generating gaseous products. Since the thermal conductivities of RDX and TNT have not yet been measured at elevated temperature, the ambient values are assumed to decrease with temperature in a manner similar to HMX and TATB, as shown in Table I. It is interesting to note that the reported thermal conductivity of RDX[19] is a factor of two lower than that of HMX despite the similarity of the two molecules. No explanation of this difference has been found in the literature.

RESULTS

The time to explosion versus reciprocal temperature curves for 0.5 inch diameter spheres in the ODTX apparatus are calculated with these chemical decomposition and thermal conduction models. For explosive mixtures the thermal conductivity and heat capacity of the unreacted explosive are assumed to be given by the mass average of the values for the individual explosives. Figure 1 shows the experimental and calculated ODTX results for TATB, LX-10, and RX-26-AF, which contains 49.3% HMX, 46.6% TATB, and 4.1% estane binder and which is assumed to be 50% HMX and 50% TATB in the calculations. The calculations

correctly predict that the time to explosion at a certain temperature is less for RX-26-AF than for LX-10, because the high thermal conductivity of TATB relative to HMX creates a faster heat flow into the HMX, which then reacts sooner than does pure HMX. If the thermal conductivity of TATB is used rather than the average HMX/TATB value, the calculated times to explosion for RX-26-AF are even less than those shown in Fig. 1.
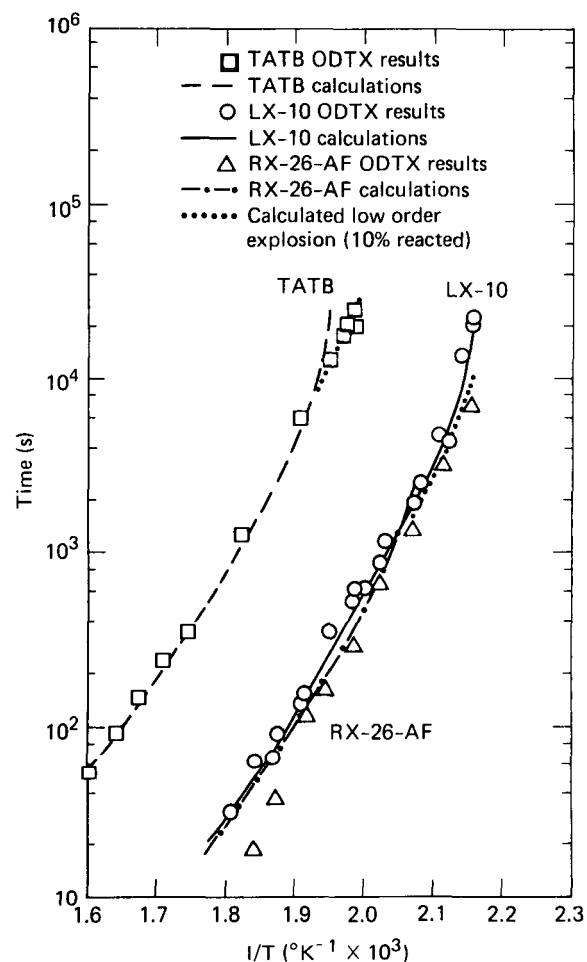

Figure 1. Experimental and calculated times to explosion for 0.5 inch diameter spheres of TATB, LX-10, and RX-26-AF.

Because the HMX in RX-26-AF is diluted with less reactive TATB, the violence of an explosion in RX-26-AF is much less than the corresponding one in pure HMX. At the lowest temperature for which an explosive event occurs in TATB and RX-26-AF, the calculations correctly predict a low order explosion in which

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1500 atm of gas pressure is generated
before thermal runaway occurs, and the
ODTX apparatus opens with little damage
to the alumninum anvils. After a study
of gaseous equations of state and the
number of moles of gas produced in each
process, a low order explosion is
assumed to occur when 10% of the
original explosive mass has been
converted to gas. This fraction always
yields more than 1500 atm independent of
equation of state or decomposition
assumptions. Actually, 6-8%
gasification is generally sufficient, as
pointed out in our previous work[2] and
in the classical work of Zinn and
Rogers.[19]

When TNT is used in the explosive
mixture instead of TATB, shorter times
to explosion for the explosive mixture
than for pure HMX at high temperatures
also occur, as shown in Fig. 2, which

contains the experimental and
calculational ODTX curves for TNT,
LX-10, and Octol (75% HMX, 25% TNT). In
this case, the thermal conductivity of
TNT is less than that of HMX. However,
since TNT is less reactive than HMX, the
reacting mixture's thermal conductivity
remains slightly higher than that of
reacting HMX, causing shorter times to
explosion at high temperatures and
longer times to explosion at low
temperatures. Except for the highest
temperatures, at which there is an
uncharacteristic amount of scatter in
the experimental data, the calculated
time to explosion curve for Octol agrees
very well with the ODTX data.

The agreement is not as good in Fig.
3 for TNT, RDX, and Comp B (modeled as
64% RDX, 36% TNT). RDX experimentally
exhibits approximately a factor of 3
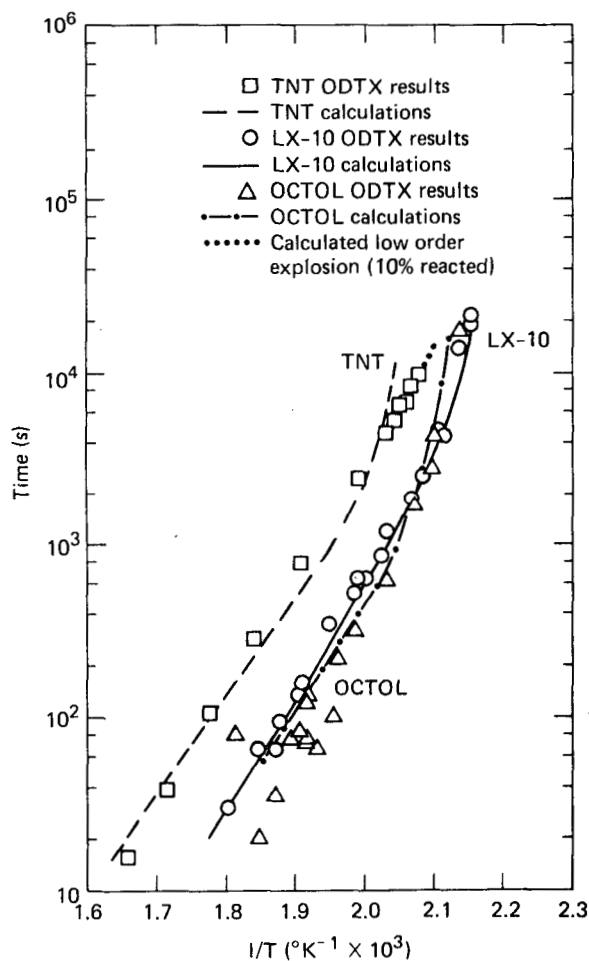increase in time to explosion just below

Figure 2. Experimental and calculated times to explosion for 0.5 inch
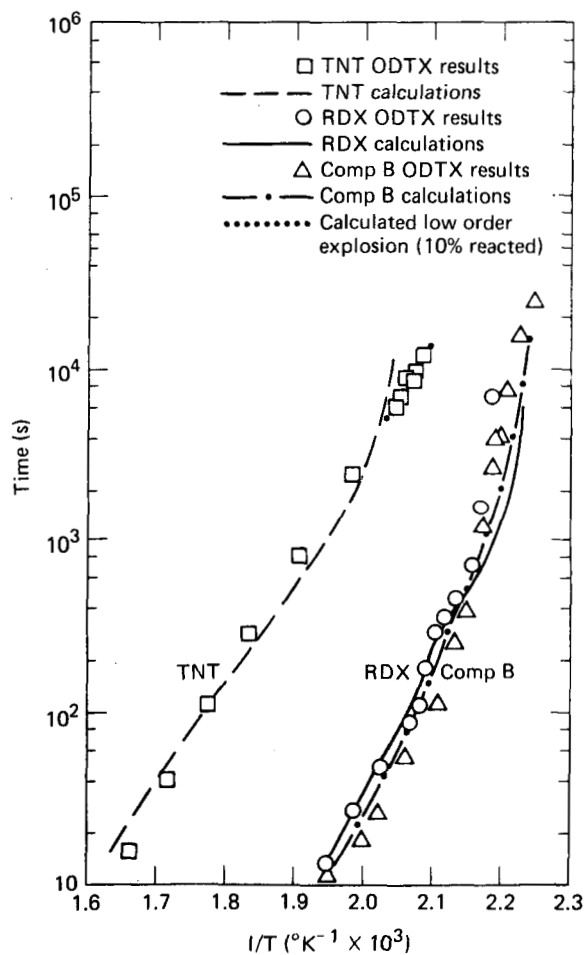diameter spheres of TNT, LX-10, and OCTOL.

Figure 3. Experimental and calculated times to explosion for 0.5 inch
diameter spheres of TNT, RDX, and Comp B.

its melting point of 204°C. The inclusion of melting in the calculations accounts for approximately a factor of two increase in time to explosion. The greater mobility of liquid RDX could conceivably increase the frequency factor for the first reaction to account for the remaining difference. This effect has not been demonstrated experimentally and therefore is not included in the calculational model. The calculated times to explosion for RDX are less than the experimental values at the lowest temperatures, and the steep increase in time to explosion near the critical temperature occurs approximately 7K lower in the calculations. The experimental times to explosion for Comp B are always slightly less than those for RDX, and the calculated curve for Comp B in Fig. 3 follows this trend at high temperatures. At low temperatures the agreement is actually better for Comp B than for RDX. While not perfect, the calculated results for time to explosion of explosive mixtures are encouraging.

An energetic binder can also cause an explosive to act as an energy generating mixture over some of its time to explosion curve. Figure 4 illustrates this effect for PBX 9404. At lower temperatures, PBX 9404 follows the LX-10 time to explosion curve, but, between 215°C-220°C in these 0.5 inch diameter spheres, PBX 9404 exhibits an order of magnitude decrease in time to explosion and LX-10 does not. As shown in Fig. 4, this effect can be calculated when the binder heat of reaction and chemical kinetics are included. It is a rather touchy situation because the binder must release sufficient energy at the right moment to accelerate the HMX reaction. Presumably an energetic binder would influence the time to explosion of the main explosive material in various ways depending on the heats of reaction and chemical kinetics of both the binder and the explosive and on the geometry and heat flow conditions of the experiment.

A major test of the time to explosion prediction capability is to calculate the results of tests with different confinement, geometry, and energy sources. A larger scale, less heavily confined explosion test which uses two inch diameter cylinders of explosive has recently been developed by Schmitz and Faubion.[21] The experimental times to explosion measured in this test for TATB (in the form of PBX 9502), LX-10, and RX-26-AF are compared with two inch diameter cylindrical geometry calculations in

Fig. 5. The calculated times are generally less than the measured times to explosion, but temperature control along these cylinders is much more difficult than in the spherical ODTX test, and a few degrees can account for the observed differences. Therefore the calculated times to explosion appear to scale well from 0.5 to 2 inch diameters.

Another new thermal explosion test which involves electron beam heating of the entire explosive sample has been developed by Stolovy et al.[22-24] Since the entire explosive sample is uniformly heated by high energy electrons, the problem of the thermal conduction of energy from an external boundary is eliminated. Thus the measured time to explosion versus heat flux into the explosive curves should be good tests of the chemical kinetic
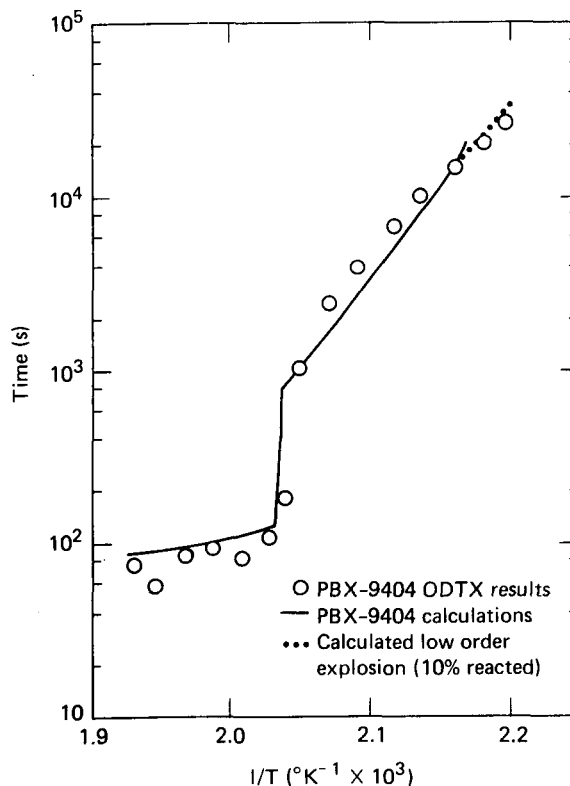

Figure 4. Experimental and calculated times to explosion for 0.5 inch diameter spheres of PBX-9404.

models. The experimental data and calculated curves for PBX 9404 and TATB are shown in Fig. 6. The calculated times to explosion are roughly a factor of two longer than the experimental times, but these calculations predict true thermal runaway in vessels that can withstand 1500 atm. The first PBX 9404 and TATB tests[22] were conducted in relatively weak aluminum cups that rupture at much lower gas pressure and thus at shorter times. When TATB is electron beam initiated in a more heavily confined apparatus that can withstand approximately 250 atm,[24] the times to explosion increase significantly, as shown by the triangles in Fig. 6, and seems to be approaching the calculated TATB curve. Electron beam thermal explosion tests should prove to be very helpful in understanding the chemical kinetics of thermal explosion.

Another new thermal explosion test that has yielded a great deal of information on internal chemical energy release rates is the spherical, unconfined heat flow oven test developed by Jaeger.[25] This test is heavily instrumented at various depths with thermocouples and can be operated for long periods to determine unconfined critical temperatures. The reactive heat flow in this unconfined test is difficult to model because the product gases escape from the reacting explosive, thus limiting the extent of any gas phase reactions and the amount of heat transfered to the explosive by the departing gaseous products. The thermal conduction history of the reacting explosive is also different from the confined system. Nevertheless, it is an important addition to the variety of thermal explosion tests that
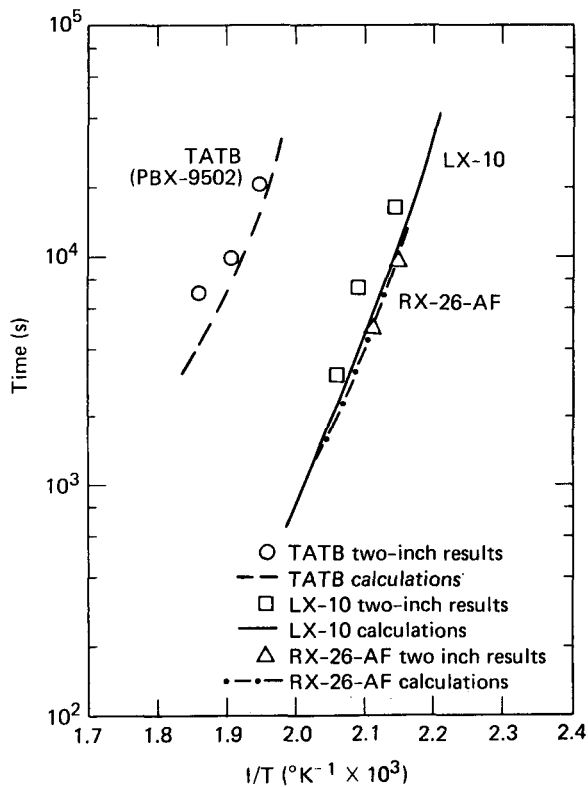

Figure 5. Experimental and calculated times to explosion for two inch diameter cylinders of TATB (PBX-9502), LX-10, and RX-26-AF.
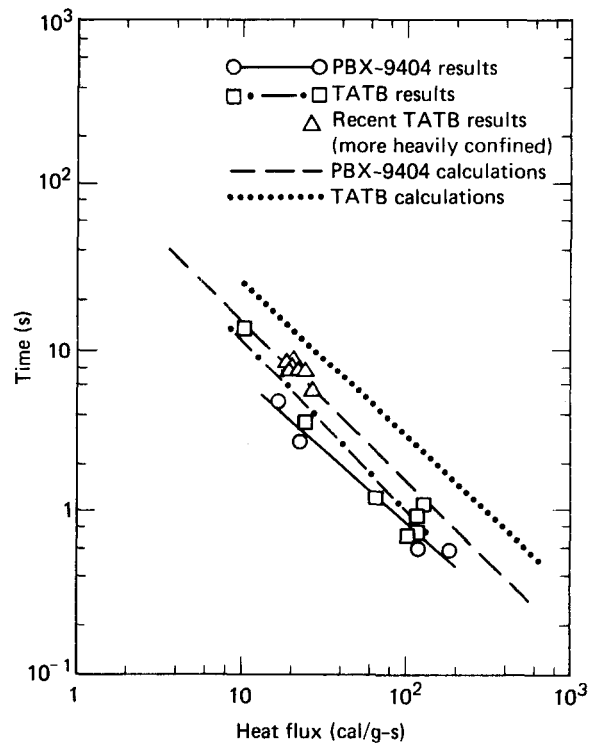

Figure 6. Experimental and calculated times to explosion for discs of TATB and PBX-9404 subjected to a high energy electron beam.

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are now producing more quantitative data on the phenomena.

CONCLUSIONS

The chemical decomposition and thermal conduction models developed for HMX, TATB, RDX, and TNT accurately predict the time to explosion versus reciprocal temperature curves generated in several heavily confined experimental geometries for pure explosives and mixtures, such as RX-26-AF, Octol, and Comp B. The effect of the energetic binder on the HMX in PBX 9404 can also be calculated . These chemical decomposition models provide useful tools for predicting explosive hazards and are based on the current understanding of the thermal decomposition process. As more mechanistic and chemical kinetic data is generated, these chemical decomposition models can be modified to improve the ability to predict the response of a high explosive to a thermal stimulus.

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