TITLE   A STUDY OF THE ROLE OF HOMOGENEOUS PROCESS IN HETEROGENEOUS HIGH
         EXPLOSIVES

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A STUDY OF THE ROLE OF HOMOGENEOUS PROCESS
IN HETEROGENEOUS HIGH EXPLOSIVES

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In a new hydrodynamic formulation of shock-induced chemical reaction, we can show formally that the presence of certain homogeneous reaction characteristics is becoming more evident as shock pressure increase even in heterogeneous high explosives. The homogeneous reaction pathway includes nonequilibrium excitation and deactivation stages prior to chemical reaction. The excitation process leads to an intermediate state at higher energy level than the equilibrium state, and as a result, the effective activation energy appears to be lower than the value based on thermal experiments. As the pressure goes up higher, the homogeneous reaction can even surpass the heterogeneous process and becomes the dominant mechanism.

INTRODUCTION

It has been recognized that various fundamental physical and chemical processes take place in the shock-induced chemical reaction of high explosives (HE).[1] Not all of them play the same significant role over a wide range of hydrodynamic condition, however. Quite often, only one becomes perhaps the dominant mechanism within a certain range while the rest are dormant or inconsequential by comparison. Wherever there is seemingly a substantial change in the appearance of reaction behavior, a switch of mechanism should be suspected. Identification of the various elementary processes and their relative contribution to the total reaction can eventually lead not only to the better understanding but also to the control of reaction behavior for specific purpose. A case in point is the variation of density and grain size on the initiability of HE.

High explosives without any form of physical heterogeneity are rarely used in applications for they are difficult to initiate; however, chemical reaction is observed when the shock intensity is high. In fact, many studies on homogeneous HE have been carried out mainly to investigate the chemical aspects without the complication associated with heterogeneity. Among the major differences observed between the shock-induced chemical reaction and the thermal reaction is that the former exhibits a lower activation energy based on a simple Arrhenius kinetics formulation,[2] considering the fact that high pressure effect alone usually inhibits chemical reaction for some major explosives.[3] The result prompts us to suspect that the chemical reaction under shock loading for homogeneous HE is beyond the simple Arrhenius kinetics.

In static loading, heterogeneity in material causes stress concentration; thus, it is not surprising to expect localization of mechanical energy dissipation under dynamic conditions. The nonuniformity of energy transformation from mechanical to thermal type results in nonuniform temperature distribution along with the associated consequence. In HE with physical heterogeneity, the response to shock loading depends on the physical structure in addition to the chemical properties. Within the HE, regions associated with heterogeneity are more susceptible to shock effect, resulting in the concentration of shock energy at some specific sites. Due to the higher energy absorption in these locations, the temperature is therefore higher than their surroundings, and chemical decomposition starts sooner. The regions with shock energy localization are called "hotspots" and serve as the center of ignition. If the hotspot burn is intense enough and if the number of hotspots is large enough, then the burning can propagate into the bulk of the HE, enabling the reaction to grow to its ultimate intensity. In this scenario, the hotspot burn is the first stage in a chain of steps that follow. As a result, the overall reaction follows the shock front quite closely. The hotspot burn itself depends on the shock intensity and also on the characteristic of the region, typically linked to the packing density as well as the grain size.

For high compaction and very fine-grained HE, however, the hotspot mechanism is not as effective at low pressure because of cooler temperatures associated with small hotspots. In this case, the initiation of HE cannot rely on the hotspot burn; an alternate route must be available if the HE can be initiated at all. The new avenue is the homogeneous process which does not require the hotspot burn as the very first step. So it is not surprising to find out that for very fine-grained and/or for high compaction HE, the initiation behavior is quite similar to that found in liquids and single crystals.[4]

The question remains how shock causes chemical reaction in homogeneous explosives. The logical answer would simply be shock heating and the reaction model follows the Arrhenius kinetics with assumed large

activation energy.[5] The driving force is just the bulk temperature. After a period of induction, a reactive wave is formed behind the shock and moves forward to catch the initial shock. Since the reactive wave has the characteristic of a detonation but travels at a greater speed than the leading shock, it is thus called superdetonation. The chemical reaction wave first falls behind the shock but gains on it until the two merge to form a single detonation wave. However, in recent experiments on nitromethane, instead of a superdetonation wave, a growing amplitude reaction wave is observed[6] and is not easily explained by the simple Arrhenius kinetics formulation. Along with the observed lower activation energy[2] and pressure effect,[3] we develop a new concept in the homogeneous reaction.

HOMOGENEOUS REACTION

High explosive element is treated as a dynamic system consisting of many degrees of freedom (modes), each with its own characteristic time. Subjected to external stress, these modes respond to the stimulus in different ways according to the times. If the longest time among all degrees of freedom is still shorter than the characteristic time of the imposing stress, then, a quasi-steady case is resulted. For example, high pressure static compression, such as found in diamond anvil experiment, can produce a temperature rise so that uniformity inside the explosive element is expected. On the other hand, if the characteristic times of some modes are longer than the characteristic time of the stimulus, these modes will not sense the effect of the stimulus until sometime later. Thus, the impact is concentrated only on those modes with shorter response times. Using shock as the mechanical stress and temperature as an indication of the effect, we expect to see faster temperature rise in some degrees of freedom and slower rise in others. As time elapses, these temperatures should converge to the equilibrium value. But before that occurs, the thermal nonequilibrium condition prevails. So we must make the distinction between a simple high-pressure state and a shock state: the former is in thermal equilibrium but the latter, at least for a period of time, is not. During the nonequilibrium period, chemical process can occur in quite a different manner. To express the higher temperature condition of those particular modes, we introduce the concept of overheat

$$\theta^{\ddagger} = F\theta. \quad (1)$$

θ is the equilibrium temperature of the medium, $\theta^{\ddagger}$ the temperature of the excited state. Evidently the overheat factor, F, is greater than 1, but it eventually approaches to 1 as the equilibrium condition reaches. If these excited modes are in the pathway to chemical reaction, using the Arrhenius kinetics formulation, a process time τ_A is expressed as

$$\tau_A = Z^{-1}\exp(\frac{\alpha}{\theta^{\ddagger}}) = Z^{-1}\exp(\frac{\alpha}{F\theta}) \quad (2)$$

Z is the frequency factor, and α the activation temperature. Since F is typically greater than 1, Eq. (2) illustrates the consequence that, expressing in term of the equilibrium temperature which is generally obtainable

from the equation of state under equilibrium conditions, the apparent activation temperature α/F would be smaller than its counterpart, α, in a normal chemical reaction. Thus we conclude that the lower activation energy appearing in shock initiation of explosives is quite likely a manifestation of a certain nonequilibrium state along the reaction pathway. Such a reduction in the activation temperature can be substantial and likely invalidates the very large activation energy condition usually assumed in asymptotic analysis. At this moment, we should point out the similarity between the heterogeneous hotspots and the nonequilibrium state discussed here, although one is acting in the microstructure level and another in the intramolecular level. To facilitate the homogeneous reaction involving an excited state, we find that the principle of the transition state theory provides an excellent framework to accommodate the formulation of shock-induced chemical reaction. Without going into any background information in great detail, we propose the following scheme:

$$R \underset{\tau_r}{\overset{\tau_x}{\rightleftarrows}} R^{\ddagger} \overset{\tau_A}{\rightarrow} P \; ,$$
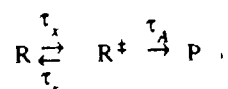
where R and P represent the reactant and the product, and $R^{\ddagger}$ the excited state of the reactant. τ_x is the excitation time for the creation of the excited state, τ_r the process time of the deactivation step. τ_A is the chemical process time based on the excited state temperature as given in Eq. (2). Based on this reaction scheme, the overall reaction rate is as follows.

$$\frac{d\lambda}{dt} = \frac{1}{\tau_H}(1 - \lambda), \quad (3)$$

with
$$\tau_H = \tau_A \left[1 + \frac{\tau_A}{\tau_x}\left(1 + \frac{\tau_x}{\tau_r}\right)\right]. \quad (4)$$

λ is the reaction fraction and t the time. τ_H is the effective global homogeneous or simply the homogeneous time. In arriving at the above result, a quasi-steady assumption is made on the excited state. Although we have constructed the reaction scheme hydrodynamically, the times τ_x and τ_r do have their quantum-mechanical origin[8]. They are treated as constant in the current formulation, or at least in the range in which they are significant. τ_x is typically in the nanosecond range. An important point to make is that τ_r can be orders of magnitude smaller than τ_x,[9] indicating that the reverse process is much faster than the excitation process. $\tau_r \ll \tau_x$, then we simplify

$$\tau_H = \tau_x\left(1 + \frac{\tau_A}{\tau_r}\right) \quad (5)$$

As seen in Eq. (2), the overheat factor F has the effect of decreasing τ_A; therefore, the amount of overheat required is to make τ_A much smaller than τ_x so that the overall reaction can proceed at a significant rate. The study of the limiting behavior of the homogeneous time leads to the conclusion that τ_H is actually composed of two times: the modified Arrhenius time

and the excitation time. Due to the Arrhenius nature of the time τ_A, at low shock pressure level, the temperature is low so that $\tau_A/\tau_r \gg 1$, and we obtain $\tau_H = \tau_A(\tau_x/\tau_r) \equiv \tau_{MA}$ which is defined as the modified Arrhenius time. The fact that τ_{MA} can be orders of magnitude larger than τ_A by the factor τ_x/τ_r is supported by the observed reduction of frequency factor Z.[2] At the other extreme where the pressure and therefore the temperature are very high, then $\tau_A/\tau_r \ll 1$ and $\tau_H = \tau_x$. Their behaviors are illustrated in Fig. 1 for TATB. The change-over pressure condition from chemical kinetic-dominated to excitation-dominated is about 320 kbar. Also shown is the conventional Arrhenius time without the overheat factor. In this paper, we do not pursue the homogeneous model alone further except to mention that we have obtained preliminary results similar to those observed in nitromethane experiments.[6] Our main goal here is to construct a unified or hybrid model including both homogeneous and heterogeneous reaction pathways, and to explore the condition for the presence of the homogeneous process and the impact on heterogeneous HE reaction behavior.

HETEROGENEOUS REACTION

Historically this model was developed first, but a peculiar behavior involving a specific characteristic time prompted us to look into a new reaction pathway in parallel to the regular heterogeneous reaction route. That particular characteristic time is related to the energy transfer between the hotspot burned product and the unburned bulk explosive, and the unusual behavior is the rapid increase of rate at high pressure. At this point, a review of the model and the refinement to account for the nonequilibrium process is deemed necessary.

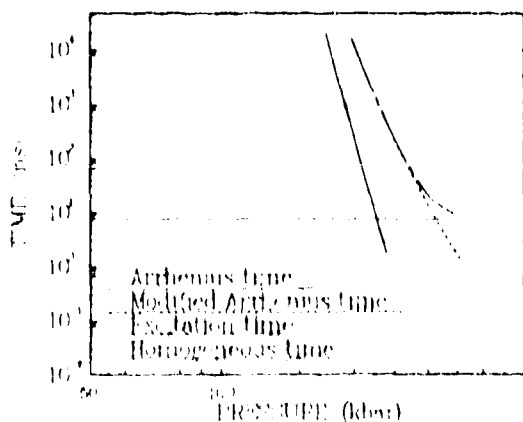In the original unified reaction model for the heterogeneous HE, we propose the following major steps:[10]

10[4]

10[3]

10[2]

10[1]

10[0]

Arrhenius time
Modified Arrhenius time
Excitation time
Homogeneous time

10[-1]

PRESSURE (kbar)

FIGURE 1 THE BASIC PROCESS TIMES IN THE HOMOGENEOUS MODEL: SIMPLE ARRHENIUS TIME τ_A, MODIFIED ARRHENIUS TIME τ_{MA}, EXCITATION TIME τ_x, AND HOMOGENEOUS TIME τ_H.
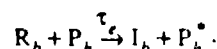
1. Hotspot shock process leading to the formation of an intermediate state, a state of higher temperature than the bulk,
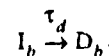
$$R_h \overset{\tau_{sh}}{\to} I_h.$$
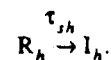
2. Hotspot decomposition, consumption of the intermediate state,

$$I_h \overset{\tau_h}{\to} P_h.$$
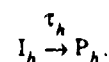
3. Heating of the bulk of explosive by the hotspot burned product, creation of the intermediate state for that region,

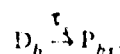$$R_b + P_h \overset{\tau_{\varsigma}}{\to} I_b + P_h^*.$$

4. Decomposition of the intermediate in the bulk of explosive, generation of decomposition product,

$$I_b \overset{\tau_d}{\to} D_b.$$

5. Decomposition product becomes final product through fast reaction,

$$D_b \overset{\tau_f}{\to} P_{bf}.$$
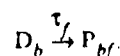
6. Decomposition product transforms into final product through slow reaction,

$$D_b \overset{\tau_s}{\to} P_{bs}.$$

The symbols R, I, D, and P represent reactant, intermediate, decomposition product, and final product. P_h represents the "cool" hotspot product. Subscripts h and b are for hotspots and bulk of explosives; f and s for fast and slow processes. The intermediate state means that it is "hot;" and the decomposition product is the direct descendant of the decomposition process but does not represent the final product. To reach the final product, there are two reaction branches, one is fast, the other slow, which accounts for the slow reactions including carbon coagulation. τ_{sh}, τ_h, τ_s, τ_d, τ_f, and τ_s represent the shock, hotspot, energy transfer, decomposition, fast, and slow process times, respectively.

After some simplifications, the above set of reaction steps leads to three rate equations for the hotspots, the bulk and the slow burn. The model worked quite well until we tried to match the interface velocity experiments where we found we had to impose a limit on the energy transfer rate.[11,12] It appears that for PBX 9502 (95% TATB, 5% Kel F), at the detonation front a rather constant reaction characteristic time of a few nanoseconds is needed. The investigation of the origin of the process at high pressure leads to the replacement of the decomposition process, step 4, by

$$I_b \overset{\tau_c}{\to} I_b' \overset{\tau_d}{\to} P_b.$$
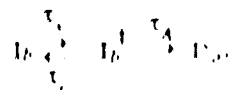
this is where we first applied the transition state principle.[13] Since the temperature of the state I_b is already quite high due to the energy transfer from the hotspot burned product, the nonequilibrium temperature associated with $I_b^{\ddagger}$ should be even higher; therefore we conclude that $\tau_A \ll \tau_r$, the reaction is dictated by the excitation process time τ_x, see Eq. (5). So instead of one rate equation for the bulk burning, we have one exclusively for the energy transfer, and followed by another for the excitation as we will see shortly.

We summarize the result here. The total reaction fraction λ is divided into three major components: hotspot, bulk reaction, slow reaction,

$$\lambda = \eta \lambda_h + (1 - \eta - \psi) \lambda_b + \psi \lambda_s. \qquad (6)$$

The designated amounts that go into the hotspots and the slow reaction are η and ψ; the balance falls into the bulk as the subscripts h, s, and b imply. The major portion is usually burned in the bulk. λ_h, λ_s and λ_b are the reaction fractions of the corresponding components, and they are zero for the completely unreacted portion and one for the burned product. Each component has its own reaction stage with a unique characteristic time. In addition to the rate equations for various reaction fractions, E_b represents the fraction of the bulk of the explosive being heated by the hotspot burned product; a quantity was considered as decomposition product previously.[10]

First, the hotspot burn,

$$\frac{d\lambda_h}{dt} = \frac{1}{\tau_h} (1 - \lambda_h). \qquad (7)$$

The hotspot process time τ_h is assumed to take the form of thermal explosion time based on the hotspot temperature which, in turn, is linked to the initial shock pressure using an empirical formulation. The calibration is essentially based on the low impact gauge records. The second stage is the energy transfer,

$$\frac{dF_b}{dt} = \frac{\eta}{\tau_e} (1 - F_b) \frac{(\lambda_h - f_0/\eta)}{(1 - f_0/\eta)}. \qquad (8)$$

Equation (8) represents the effect of energy transfer from the hotspot burned product to the unburned explosive. τ_e/η is the characteristic time for overall energy transfer, including the hotspot mass fraction effect, the amount of heat source f_0 represents a threshold condition. Even though the energy transfer mechanism is not known and cannot be modeled directly, it is probably through conduction at low pressure level but becomes turbulent mixing at high pressure. That is the reason why we choose to relate the energy transfer time to pressure. The method is similar to the burn rate for solid propellants. The calibration is done based on the wedge test results (Pop plot) similar to the Forest Fire rate.

The chemical process is controlled by the excitation process after the energy transfer stage,

$$\frac{d\lambda_b}{dt} = \frac{1}{\tau_x} (F_b - \lambda_b). \qquad (9)$$

and finally, the slow reaction follows the bulk burn,

$$\frac{d\lambda_s}{dt} = \frac{1}{\tau_s} (\lambda_b - \lambda_s). \qquad (10)$$

Calibration of τ_x, τ_s and ψ is achieved by matching interface velocity and plate push experiments. Figure 2 shows the variations of the hotspot process time τ_h, the overall energy transfer time τ_e/η, the excitation time τ_x, and the slow process time τ_s with respect to the change of the hydrodynamic condition represented by pressure, for PBX 9502. We can draw the conclusion that the hotspot process controls the rate in the lowest pressure range. As the pressure goes up higher, the energy transfer becomes the limiting factor. These two processes dictate the initiation behavior of the HE. In the detonation phase, the reaction is essentially controlled by the nonequilibrium excitation, Eq. (9). The slow reaction, Eq. (10), affects the late time behavior, and contributes to the nonsteady detonation phenomenon.[14]

One feature standing out quite vividly is the rapid decrease of the overall energy transfer time at the high pressure level, even in log-log scale. Such a strong hydrodynamic dependence through pressure is suspected - perhaps too strong to be physically reasonable. We currently use the following relation,

$$\tau_e = [G_0 \ p + \exp(\Sigma a_i \ p^i)]^{-1}. \qquad (11)$$

where G_0 and a_i are constant. The exponential part is known as the Forest Fire with typically more than ten terms. Such a complex expression is used to accelerate the rate in the high pressure region, a condition required to match the Pop plot. The formulation quite likely misrepresents the physical origin, that is, the energy transfer as we intend it to be. If a simpler power law is used to express the energy transfer, for example,
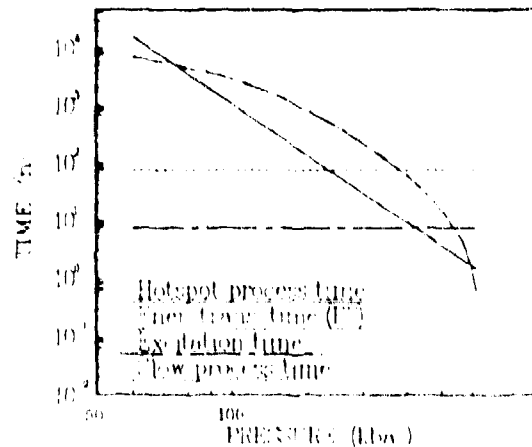
FIGURE 2 THE FOUR MAJOR PROCESS TIMES IN THE HETEROGENEOUS MODEL. HOTSPOT PROCESS TIME τ_h, OVERALL ENERGY TRANSFER TIME τ_e/η, EXCITATION TIME τ_x, AND SLOW PROCESS TIME τ_s.

$$\tau_e = (G_0 \, p + G_n \, p^a)^{-1}, \qquad (12)$$

where G_n and a are constant obtained by fitting the lower pressure portion of Eq. (11). The results are shown in Fig. 3. Since Eq. (12) yields a lower rate than Eq. (11) in high pressure, a compensation must be made to account for the difference between the two. The logical and physically sound choice is to add a new branch in parallel to the heterogeneous branch. This new pathway has to be of the homogeneous type which does not require hotspot burn and certainly becomes effective only at high pressure level. However, a simple Arrhenius time, also shown in Fig. 3, would not work since it would produce too fast a reaction rate; therefore, we conclude that the proper homogeneous time must be the one we have presented previously. At this point, we cannot speculate on the adequacy of the form of Eq. (12), but for the time being, it does serve the purpose and it is simple in form.

HYBRID MODEL

We believe the homogeneous process does contribute to the reaction even for heterogeneous high explosives, but its presence is felt mainly at high pressure. Realizing this fact, however, we should not generate a new set of rate equations by simply adding the two rates together as given in Eq. (3) and Eqs. (7) through (10). A formal treatment of multiple reaction stages involving both branches must be carried out. In addition to the heterogeneous pathways 3 and 4 as seen earlier, we add a new branch for the bulk of explosive,

$$R_h \; \underset{\tau_r}{\overset{\tau_e}{\rightleftarrows}} \; R_b \; \overset{\tau_A}{\rightarrow} \; D_b.$$
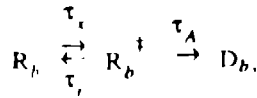
here we assume the homogeneous reaction affects the

bulk of explosive only. After extensive mathematical manipulation, Eqs. (8) and (9) are replaced by:

$$\frac{dE_b}{dt} = (1 - E_b)\left[\frac{\eta}{\tau_e} \frac{(\lambda_h - f_0/\eta)}{(1 - f_0/\eta)} + \frac{1}{\tau_H} \right] , \quad (13)$$

and

$$\frac{d\lambda_b}{dt} = \frac{1}{\tau_x}(E_b - \lambda_b) + \frac{1}{\tau_H}(1 - E_b)\left(1 - \frac{\tau_A}{\tau_x}\right). \quad (14)$$

τ_H is the characteristic time of the homogeneous branch defined previously in Eq. (5). The second terms on the right-hand sides of Eqs. (13) and (14) represent the additional contribution due to the homogeneous process. Its presence in Eq. (13) makes the apparent energy transfer time shorter or the rate faster as reflected in the original formulation using the Forest Fire expression. It should be noted that the benefit of the homogeneous contribution to the decomposition product is not realized until τ_A is smaller than τ_e. However, the homogeneous pathway does not require any precursor burn from the heterogeneous hotspots as indicated in the burn rate. It should be emphasized that although the homogeneous time τ_H appears to link to the pressure, in fact, the relationship is to the temperature through τ_A as given in Eq. (2). It is through this particular connection that the homogeneous process remains effective longer as we will see later. Overall, we find that τ_h and τ_e and the hotspot mass fraction η are affected exclusively by the physical microstructure, whereas τ_x, τ_r, τ_A, and τ_r and the slow mass fraction ψ are intrinsic to the fundamental molecular chemical property. For granular explosives, the heterogeneous process is essentially a surface burn mechanism, whereas the homogeneous branch directly affects the interior. Figure 4 shows all the principal process times in the hybrid model.
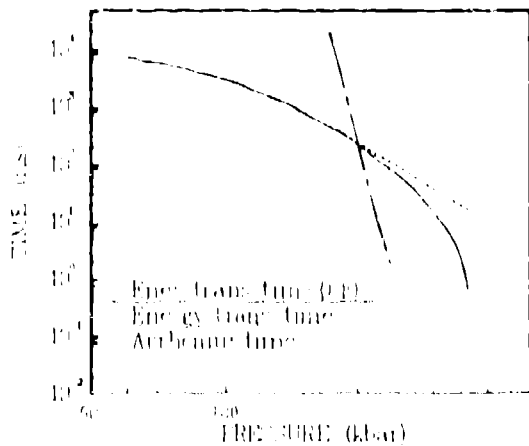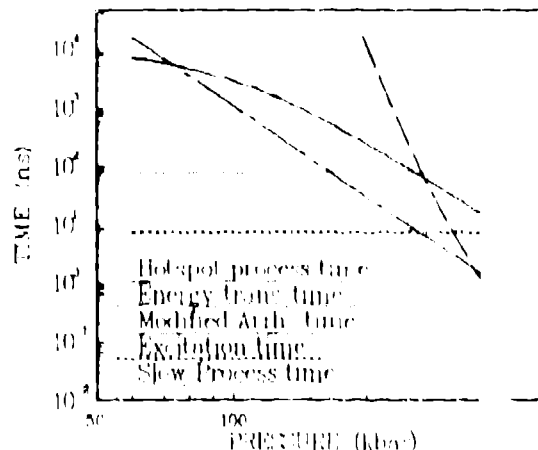

FIGURE 3. THE ENERGY TRANSFER TIME BASED ON THE FOREST FIRE, THE NEW ENERGY TRANSFER TIME, AND THE SIMPLE ARRHENIUS TIME

FIGURE 4. ALL MAJOR PROCESS TIMES IN THE HYBRID MODEL.

SIMULATION OF THIN EXPLOSIVE CHARGE EXPERIMENTS

Since the contribution of the homogeneous process is significant only in the high pressure regime, its presence can only be indirectly implicated in hydrodynamic experiments near detonation phase. Although the interface velocity experiment on very thin explosives was designed for other purpose,[15] it does provide an excellent opportunity to test the hybrid model. The reason will be made clear shortly. A very thin HE in the range of 0.25 mm and up was initiated by a driver consisting of a planewave lens, a piece of Comp B and a layer of aluminum. The driver provides a near prompt initiation on PBX 9502. The HE charge was sandwiched between the aluminum and a transparent window of potassium chloride (KCl). Measurement of the interface velocity between the HE and the window was made using the Fabry-Perot technique. Two calculations are made in each case: one based on the original heterogeneous model with the Forest Fire expression for the energy transfer time (dash curve), and another using the hybrid model with the simplified energy transfer time relation and with the homogeneous process explicitly included (solid curve). Markers are from experiments. Result is presented in Fig. 5 for a thickness of 0.25 mm. Instead of a sharp peak observed in thicker HE, a rounded top is seen in the experimental record. This feature indicates the decreasing reaction rate due to the quenching effect even with a very strong initial shock. The heterogeneous model calculation seems quite satisfactory and captures all the features including the reverberation inside the HE, but it still slightly underestimates the experiment. With an adequate amount of overheat, the result of the hybrid model matches the experiment almost perfectly. In this configuration, it is realized that although the HE is initiated rather promptly by the driving system, the reaction cannot really sustain itself to reach the final detonation due to the pressure release, causing rapid

reaction rate reduction. If the reaction is solely supported by the energy transfer process through the pressure dependence in the pure heterogeneous reaction model, then indeed the reaction would drop rather quickly, and so does the velocity as seen in simulation. However, even with significant pressure drop, the temperature decrease would not be as great. As a result, the temperature condition can support reaction by the homogeneous reaction pathway, in the hybrid model. With a proper amount of overheat, the net result is additional growth in reaction intensity as reflected in the interface velocity record. For increasingly thicker HE charges, 0.5 mm, 1.0 mm, and 2.0 mm, seen in Figs. 6, 7, and 8, the rounded top feature gradually diminishes as the two different model calculations converge. Although there is no significant difference between the two simulations numerically, the important point to make is the better representation of the physical phenomenon in the high pressure region using the hybrid model.
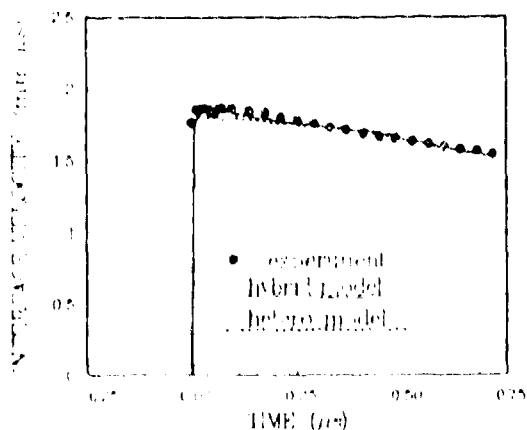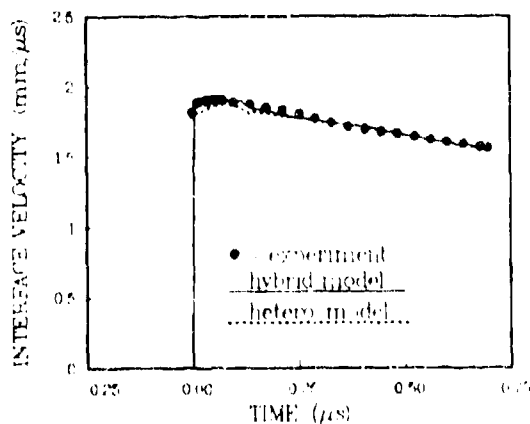

FIGURE 6. 0.5-MM PBX 9502, EXPERIMENT AND CALCULATIONS

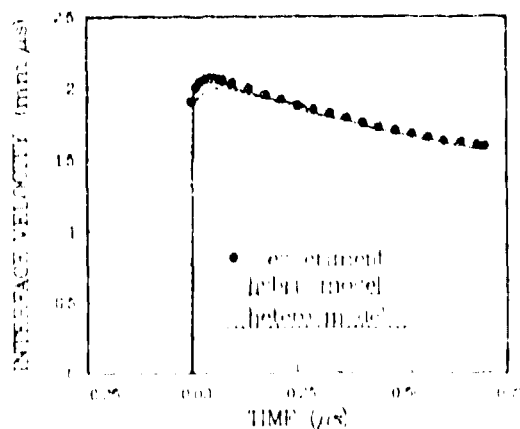FIGURE 5. 0.25 MM PBX 9502, EXPERIMENT AND CALCULATIONS

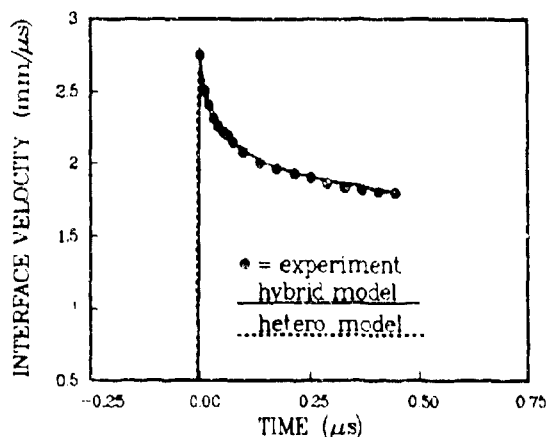FIGURE 7. 1.0 MM PBX 9502, EXPERIMENT AND CALCULATIONS

FIGURE 8. 2.0-MM PBX 9502, EXPERIMENT AND CALCULATIONS

CONCLUSIONS

Based on the process time characteristics, we can identify the significance of various fundamental processes in different h. drodynamic regimes. For heterogeneous explosives, the low pressure initiation behavior is controlled by the hotspots and followed by the energy transfer. The homogeneous branch works in parallel to the heterogeneous branch. Although limited mainly in the high pressure regime, the homogeneous process does contribute to the total reaction. Its effectiveness, however, relies on the nonequilibrium condition associated with shock. A novel idea to account for this effect is introduced by using the concept of overheat. The overheat factor represents the ability of a few selective modes to absorb the shock energy more effectively than others; and the excitation time is a measure of how fast that can be accomplished before equilibration settles in. The equilibration process is characterized by the deactivation process time. As the pressure gets higher, the reaction rate is first controlled by the modified Arrhenius process but eventually reaches a plateau dominated by the excitation process. Further increase in shock strength would not increase the rate. Finally, a slow reaction component appears following the main burn. The appearance of a strong pressure dependence in energy transfer using the Forest Fire formulation seems to be an attempt to accommodate the effect of the homogeneous process.

ACKNOWLEDGMENTS

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