

*Transition State Theory
Applying to the Study of
Reaction Processes in Detonation*

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**TRANSITION STATE THEORY
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IN DETONATION**

by
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ABSTRACT

The presence of a nearly constant process time that characterizes the fast reaction portion found in the detonation of condensed high explosives can be explained by the transition state theory. Through hydrodynamic modeling, we identify that time as the excitation time for the production of an energetic state that can go either forward to achieve decomposition or backward to the original unexcited state. The energetic state is a representation of a nonequilibrium condition that favors the chemical reaction, whereas the unexcited or equilibrium state does not. This process time is determined by matching the experimental interface velocimetry record, and its value is nearly constant over a wide range of conditions.

INTRODUCTION

Detonation of high explosives involves complex physical phenomena and chemical transformations; we are unable even to describe some of the essential ones. From time to time an ambitious project is proposed to formulate the problems according to all known basic principles, but reality denies us the power to achieve absolute understanding. Practical problems, however, need to be solved. The alternative is phenomenological modeling based on extensive experimental evidence and physical reasoning. We have been quite successful in the hydrodynamic simulation by using the characteristic or process time concept, but often we sacrifice the chemical and physical detail of some specific times. With the

availability of new experimental evidence and more fundamental results based on molecular dynamics and quantum-mechanical works of molecular level, we must revise the interpretation along with new formulation. The work presented in this report is such an effort.

In the course of studying the detonation-wave reaction zone behavior, we find it necessary to impose a condition in which the process time, representing the fast reaction portion in the multistage process model, is nearly a constant even though the pressure varies substantially in that thin region. Actually, the characteristic time is almost independent of the local hydrodynamic condition as exhibited in both the interface velocity experiments and simulations using different window materials.^(1,2) This condition of weak dependence on pressure is believed to be caused by the change in the decomposition mechanism, notably the decrease of activation energy,⁽³⁾ and in the nature of the multistage process in general.⁽⁴⁾ However, the origin of that characteristic time has not been fully explored and is said only to be decomposition related.⁽¹⁾ Evidence of low activation energy abounds, as presented in many studies of shock initiation of high explosives using Arrhenius type kinetics^(5,6) and compared to the normal thermal decomposition value.⁽⁷⁾ High pressure can affect chemical kinetics through the change of activation volume, but acceleration in reaction rate can be achieved only if there is a definitive decrease in the activation volume, which is unlikely in the decomposition of typical solid explosives unless some initial crucial steps provide this condition.⁽⁸⁾ It should be noted that the decrease of activation volume is equivalent to the decrease of activation energy, or more precisely, the decrease of activation enthalpy. In fact, the study of HMX (cyclotetramethylene tetranitramine) indicates the trend of deceleration in reaction rate of high pressure.⁽⁹⁾ Therefore, we cannot conclude that high pressure compression alone can always change the reaction rate in favor of decomposition. However, in the case of shock compression, the acceleration of chemical reaction is always seen. This accel-

erated reaction leads us to the question of what happens when shock is applied to explosives. The effect is more than just high pressure.

We view high explosive as a dynamic system. In responding to external stimulus, various degrees of freedom (modes) can follow the stimulus quite closely if the stimulus is nearly static. To place this idea in a different context, when the longest relaxation time among all degrees of freedom is still shorter than the characteristic time of the stimulus, the system can respond to the stimulus quickly. In this case we say the system is in equilibrium within itself and with its stimulus. For example, high static compression, such as a diamond anvil experiment, can result in such a temperature rise that uniformity inside the explosive is expected. On the other hand, if the characteristic time of the stimulus is short in comparison with the relaxation times of some degrees of freedom, those degrees of freedom with longer relaxation times do not see the effect of the stimulus until sometime later. The result is that the effect is concentrated on those degrees of freedom with shorter relaxation times. Using shock as the stimulus and temperature as an indication of the effect of the stimulus, we expect to see faster temperature rise in some degrees of freedom and slower temperature rise in others. Therefore, at the onset of shock, higher translational temperatures but cooler vibrational temperatures generally result because the former have shorter relaxation time but the latter longer. It is important to note that decomposition is associated with vibrational excitation. As time elapses, these temperatures should converge to the equilibrium value. But before that convergence, the thermal nonequilibrium condition prevails. So we must make the distinction between the simple high-pressure state and the shock state: the former is in thermal equilibrium but the latter, for a period of time, is not. During the nonequilibrium period, developments can occur in quite a different manner. Contribution of the nonequilibrium effect because of electronic excitation is seen in laser initiation of high explosives⁽¹⁰⁾ and laser enhancement of initia-

tion,⁽¹¹⁾ with evidence given through the influence of wavelength. Electronic excitation is believed to enhance decomposition.^(3,11) Under shock compression, the electronic excitation is easily accomplished following the translational excitations;⁽⁴⁾ in turn, the excited electronic state can alter the vibrational modes. If such a modification is beneficial to decomposition, then reaction of very high rate can be realized. Although early works are inclined to conclude that activation energy lowers because of electronic excitation,^(12,13) recent thinking moves toward the idea of higher temperature.^(3,11) Using Arrhenius kinetics, these two are essentially equivalent, as we will see later. The objective of this report is not to identify any particular mode that takes the fastest route leading to decomposition, but rather to accept the concept that such a mode does exist and represents a nonequilibrium state. Certainly this state has more energy than it would under an equilibrium condition, and therefore, the temperature of that state is hotter than the equilibrium value. To express its hotness relative to the equilibrium value, we introduce the concept of overheat:

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

θ is the equilibrium temperature of the medium, θ^\ddagger the temperature of the energetic state. Superscript \ddagger indicates a nonequilibrium or more energetic condition. Evidently F , the overheat factor, is greater than 1, but it eventually approaches to 1 as the equilibrium condition is finally reached. Using the simplest Arrhenius kinetics relation, instead of the customary chemical reaction rate formulation, a process time τ_a is expressed as

$$\tau_a = Z^{-1} \exp\left(\frac{\alpha}{\theta^\ddagger}\right). \quad (2)$$

Z is the frequency factor, α the activation temperature. In terms of the equilibrium temperature θ , we obtain

$$\tau_a = Z^{-1} \exp\left(\frac{\alpha}{F\theta}\right), \quad (3)$$

or

$$\tau_a = Z^{-1} \exp\left(\frac{\alpha^\ddagger}{\theta}\right), \quad (4)$$

with

$$\alpha^\ddagger = \frac{\alpha}{F}. \quad (5)$$

Since F is typically greater than 1, α^\ddagger is always less than α . Equation (4) demonstrates that if we insist on using the equilibrium temperature, which is generally obtainable from the equation of state under usually equilibrium conditions, then the apparent activation temperature α^\ddagger must be smaller than its counterpart in normal decomposition. Thus we conclude that the lower activation energy appearing in shock initiation of explosives is a manifestation of a certain nonequilibrium state that leads to a faster reaction pathway.

Since the nonequilibrium state plays a central role in determining the shocked-induced chemical reaction, its place is similar to the activated complex that appears in the transition state or activation complex theory for expressing the formation of an energetic state so that a potential barrier can be overcome in order to achieve chemical reaction.^(14,15) The essence of the theory is that the energetic state is in chemical equilibrium with the reactant. This theory is broadly used to interpret the effect of pressure on the chemical reaction rate and to show the role of the change of activation volume.^(16,17,18) We will not elaborate the theory any further in this report. A recent study on initiation of crystal applies this theory from quantum-mechanical con-

sideration,⁽¹⁹⁾ and we draw parallels as well as conclusions from that study to help in formulating the current hydrodynamic model.

REACTION KINETICS

We address the problem of reaction kinetics in a sequential manner, from the reaction of hot spots, to the propagation of the reaction into the bulk of explosive, and finally to the slow reaction. The original hot spot reaction model^(20,21) for the initiation of heterogeneous high explosive was expanded into the detonation regime with broader physical insight and wider application.⁽²²⁾ The dominant new feature is the two characteristic times: a fast one, which has a weak pressure dependence near the detonation wave front, and a slow one, which is essentially constant.^(1,2) Instead of simply imposing a limiting value on the fast reaction rate, we include in this study a special stage in which the energetic or non-equilibrium state appears formally, and the origin of the nearly constant fast reaction time is identified.

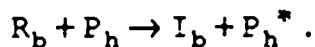
In the unified model of shock-induced chemical reaction of explosives, we divide the total reaction fraction λ into three main components: hot spots, bulk reaction, and slow reaction,⁽²²⁾

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

η and ψ designate the absolute amounts in fractions that go into the hot spots and slow portion; the rest is, of course, burned in the bulk as the subscripts h , s and b imply. Thus λ_h , λ_s and λ_b are the reaction fractions in each of the stages. For this study, we ignore the detail of hot-spot burn and assume it has reached completion, $\lambda_h = 1$, so that Eq. (6) becomes

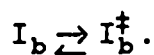
$$\lambda = \eta + (1 - \eta - \psi)\lambda_b + \psi\lambda_s. \quad (7)$$

The symbols R, I, T, and P are used to represent reactants, intermediates, transition products, and final products. Following the hot-spots burn, the bulk reaction begins with the heating of the reactant by the hot-spot burned product, thus forming an intermediate state for that region; the intermediate state I_b is in thermal equilibrium,



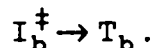
P_h^* represents a cooler P_h after energy transfer from the hot spots to the bulk of explosive. In this reaction, the characteristic time is τ_e , representing the aspect of energy transfer.

The new stage added in the bulk reaction is the formation of non-equilibrium or energetic state, a pre-decomposition stage,



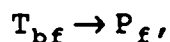
I_b^\ddagger represents a state of nonequilibrium or higher excitation level because of shock action. Significantly, this stage shows not only the presence of the energetic state but also the backward process that allows the energetic state to return to the equilibrium condition. Again, using temperature as an indication of the energetic level, we say that I_b^\ddagger is at a higher temperature than I_b . To characterize the forward and the backward processes, we use τ_x as the excitation time and τ_r as the relaxation time.

From the energetic state, the explosive decomposes into products of transitional nature:

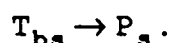


Here τ_a is the characteristic time of the Arrhenius type; namely, its dependence on temperature follows the Arrhenius relation. The

reason for the inclusion of transition products is as follows. We recognize that although the chemical process in the bulk of explosive is mainly decompositional, some recombinations will occur, particularly near the end of the reaction. A most prominent one is solid carbon coagulation (or condensation); the process is exothermic and slow. The exothermic aspect allows us to include its contribution to the total reaction, but the process time can be quite long and cannot be ignored. Rather than taking the decomposition products as final, we assume them to be transitional (or partially reacted), with two different kinds: one goes to the final form rather quickly, but the other takes considerably longer to reach the final state, as in, for example, very large carbon molecules. Accordingly, we have two parallel steps following decomposition: First, the transition product becomes the final product through a fast reaction,



and second, the transition product transforms into final product through a slow reaction,



The characteristic times of the fast and slow post-decomposition stages are τ_f and τ_s , respectively.

The rate equations for all the reaction steps are summarized below.

$$\frac{dR_b}{dt} = -\frac{\eta}{\tau_e} R_b, \quad (8)$$

$$\frac{dl_b}{dt} = \frac{\eta}{\tau_e} R_b - \frac{l_b}{\tau_x} + \frac{l_b^\ddagger}{\tau_r}, \quad (9)$$

$$\frac{dl_b^\ddagger}{dt} = \frac{l_b}{\tau_x} - \frac{l_b^\ddagger}{\tau_r} - \frac{l_b^\ddagger}{\tau_a}, \quad (10)$$

$$\frac{dT_{bf}}{dt} = \frac{l_b^\ddagger}{\tau_a} - \frac{T_{bf}}{\tau_f}, \quad (11)$$

$$\frac{dT_{bs}}{dt} = \frac{l_b^\ddagger}{\tau_a} - \frac{T_{bs}}{\tau_s}, \quad (12)$$

$$\frac{d\lambda_b}{dt} = \frac{T_{bf}}{\tau_f}, \quad (13)$$

and

$$\frac{d\lambda_s}{dt} = \frac{T_{bs}}{\tau_s}. \quad (14)$$

The conservation requirement adds more algebraic relations and is not repeated here.⁽²²⁾ Since most of the reaction follows the fast post-decomposition reaction route, we use λ_b instead of λ_f in Eq. (13).

An additional feature in applying the transition state theory is the assumption of quasi-steadiness for the energetic state I_b^\ddagger . The production and the consumption are approximately balanced out, so that from Eq. (10),

$$\frac{dl_b^\ddagger}{dt} = 0; \quad (15)$$

thus

$$I_b^\ddagger = \frac{I_b}{\tau_x} \frac{1}{\left(\frac{1}{\tau_a} + \frac{1}{\tau_r}\right)}. \quad (16)$$

The assumption about the smallness of τ_f as compared to τ_a leads to the conclusion that T_{bf} must be quite small.⁽²²⁾ Defining $E_b = 1 - R_b$ and after some manipulations, we have

$$\frac{dE_b}{dt} = \frac{\eta}{\tau_e} (1 - E_b), \quad (17)$$

$$\frac{d\lambda_b}{dt} = \frac{1}{\tau_c} (E_b - \lambda_b), \quad (18)$$

with

$$\tau_c = \tau_x \left(1 + \frac{\tau_a}{\tau_r}\right) + \tau_a, \quad (19)$$

and

$$\frac{d\lambda_s}{dt} = \frac{1}{\tau_s} (\lambda_b - \lambda_s). \quad (20)$$

Contrary to previous formulation,^(1,2) a rate equation for an intermediate quantity E_b is explicitly required. Equations (17) and (18) are essentially equivalent to the expression of

$$\frac{d\lambda_b}{dt} = \frac{i}{\tau_b} (1 - \lambda_b), \quad (21)$$

with

$$\tau_b = \max(\tau_c, \tau_e/\eta) \quad (22)$$

presented in early work.^(1,2) Extensive numerical computation shows no difference using either the complete formulation, Eqs. (17) and (18), or the simplified version, Eqs. (21) and (22). τ_c is a constant of 5 ns for some TATB (triaminotrinitrobenzene)-based explosives and is determined by matching hydrodynamic experimental data.^(1,2)

Let us examine Eq.(19) further. First, since τ_a is evaluated at a temperature higher than the equilibrium value which is already quite high because of energy transfer from the hot-spot product, it is very likely that τ_a is in the sub-nanosecond range, and we can assume

$$\tau_a \ll \tau_x. \quad (23)$$

Second, the relaxation time τ_r for the backward process must be longer than or at least the same order of magnitude as the excitation time τ_x if any significant forward reaction results. In conjunction with the previous assumption, the condition puts

$$\tau_a \ll \tau_r, \quad (24)$$

and thus we conclude $\tau_c \approx \tau_x$. (25)

Here we identify the origin of the constant fast characteristic time τ_c in the reaction being the excitation time τ_x for producing an energetic state that is critical in shock-induced decomposition. A similar time in a quantum-mechanical view is obtained. It is the time for phonon-to-vibron energy transfer and is found to be nearly constant also.⁽¹⁹⁾ Thus a link between the phenomenological formulation based on the nonequilibrium concept and the

quantum-mechanical conclusion is established. It should be quite clear that without the assistance of hot-spot burn, τ_d may not be small enough to be ignored and thus τ_c becomes greater than τ_x as expressed in Eq.(19). This condition explains why homogeneous materials are much harder to initiate even with the beneficial effect of nonequilibrium. Finally, τ_s is taken as constant, and τ_c has a strong pressure dependence,⁽²²⁾ but its effect is minimal in the detonation phase.^(1,2)

EXPERIMENTS AND SIMULATIONS

We shall examine one particular TATB-based explosive: PBX 9502, which contains 95% TATB and 5% Kel-F 800 (chlorotrifluoroethylene/vinylidene fluoride copolymer). Since we are not able to probe the interior of high explosive under detonation conditions without introducing some degree of interference, an alternate is used: interface velocimetry. The interface velocity between a sample high explosive and a transparent window is measured and also calculated using both the reaction model presented earlier and an appropriate equation of state. Certainly the window material would impart some effect on the detonation condition, but for our purpose of looking for "constants", different window materials are even better: LiF (lithium fluoride), KCl (potassium chloride), and PMMA (polymethylmethacrylate) are to provide impedance of high, medium, and low values relative to PBX 9502. If the time parameters τ_c and τ_s are truly constant and τ_c has weak pressure dependence, the calculations should show whether this is the case by comparison with experiments. To initiate the HE sample, we use a plane wave lens, 25-mm Composition B, and then a 10-mm aluminum plate. Between the HE sample and the window, the interface is vapor-coated with submicron-thick aluminum to reflect the laser beam. A Fabry-Perot interferometer is used to produce interference fringe. Detail on the experiments is given in Reference 2.

Calculation is made using the following input: $\eta=0.003$, $\psi=0.15$, $\tau_c=5$ ns, and $\tau_s=75$ ns for PBX 9502. The expression for the dependence of τ_c on current and local hydrodynamic condition

through pressure is rather complicated; ⁽²²⁾ the effect is minimal in the current study, but it can be seen in short duration initiation which gives strong pressure relief. ⁽¹⁾ The experimental and numerical results of the interface velocity are presented in Figures 1 through 6 using three different window materials mentioned earlier and for two different explosive charge lengths: 13 mm and 50 mm. Very good agreement is found between experiment and simulation. Computationally as well as experimentally, the initial spike peak that corresponds to a non-reacted shock condition (von Neumann spike) is difficult to handle. We see consistent increase in calculated peak value but not in experiments when the charge length increases. We believe there is a slight increase in detonation velocity correspondingly, but the amount of increase is extremely difficult to compute. Accurate detonation velocity measurement is available only by using a long rate stick when the detonation reaches truly steady state; therefore we cannot exclude the growth aspect of detonation velocity in the experiments we describe here. Finally, we find from the reproducibility study that shock properties of PMMA are not reliable. This unreliability explains the discrepancy between experiment and calculation when PMMA window material is used, particularly for a shorter explosive charge length. Another explanation is the deficiency of the equation of state for PBX 9502 in the low-pressure regime, evidenced further in plate push experiments when aluminum plate is used. ⁽²³⁾

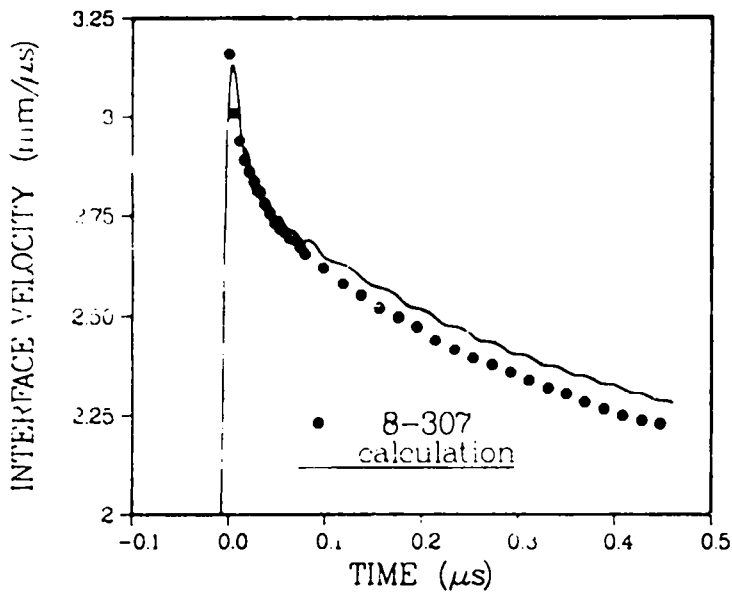


Fig. 1. Interface velocity between PBX 9502 and PMMA window, 13-mm charge length.

Fig. 2. Interface velocity between PBX 9502 and PMMA window, 50-mm charge length.

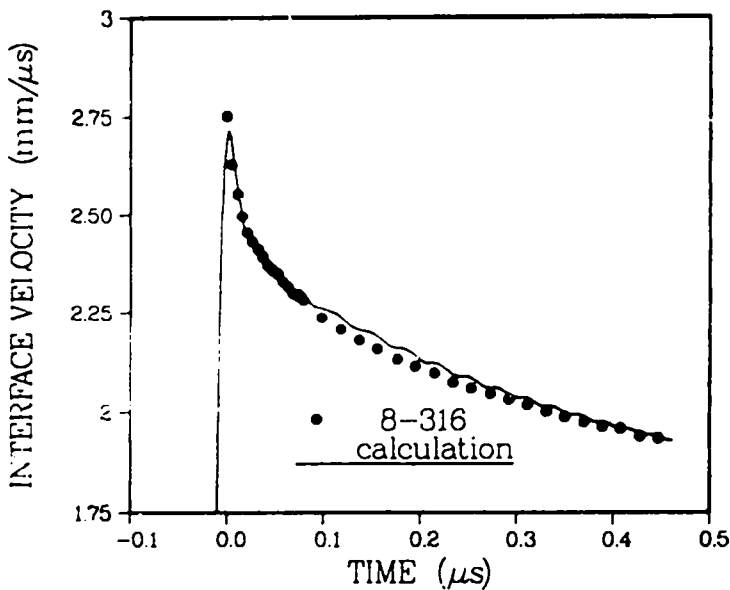
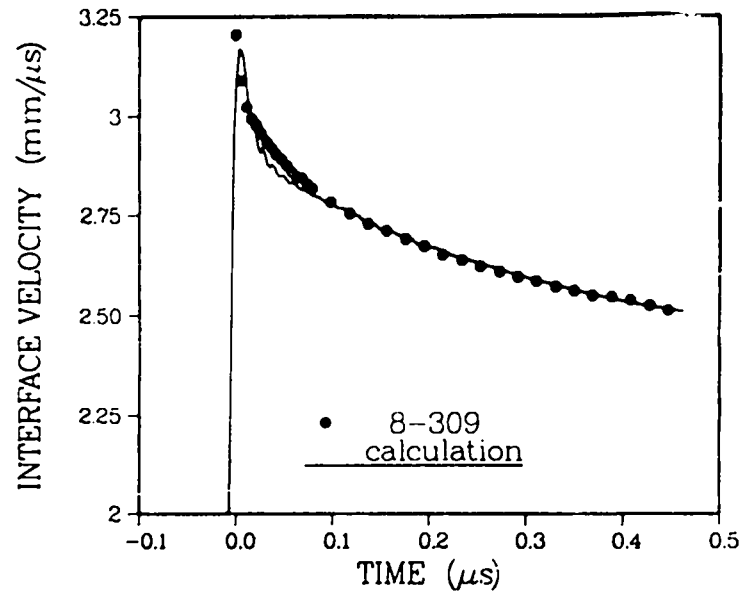


Fig. 3. Interface velocity between PBX 9502 and KCl window, 13-mm charge length.

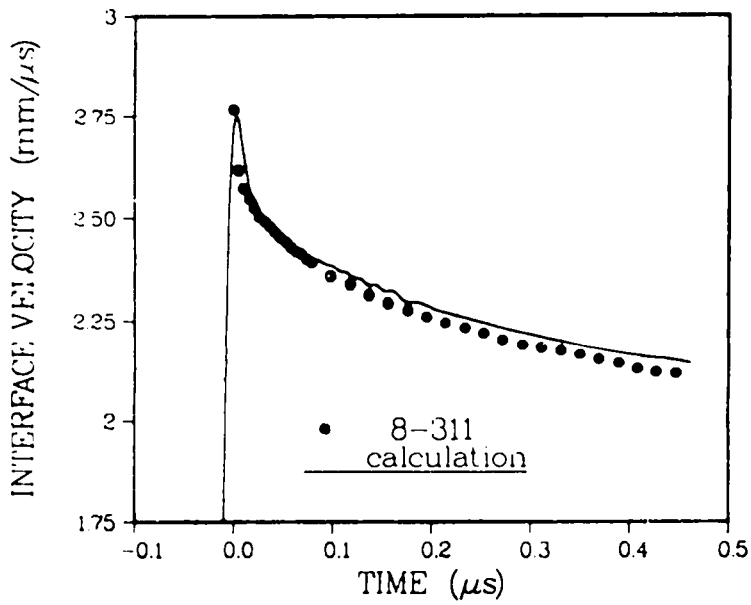


Fig. 4. Interface velocity between PBX 9502 and KCl window, 50-mm charge length.

Fig. 5. Interface velocity between PBX 9502 and LiF window, 13-mm charge length.

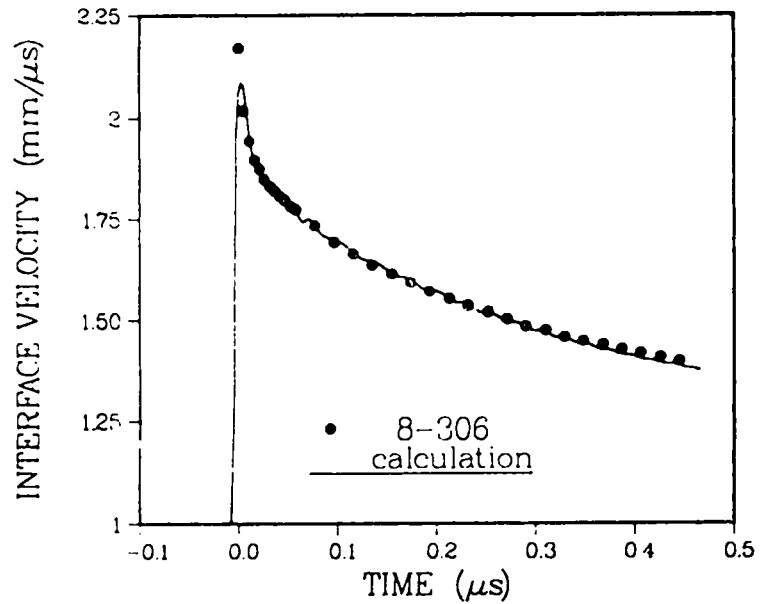
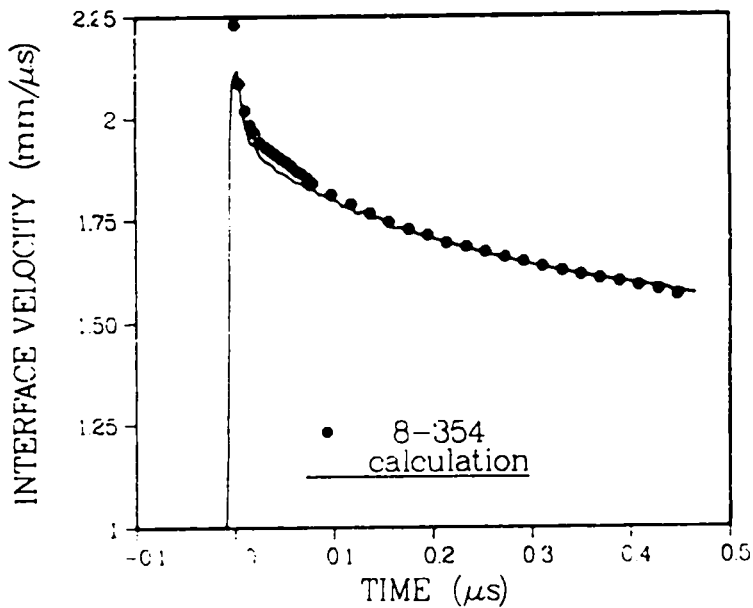


Fig. 6. Interface velocity between PBX 9502 and LiF window, 50-mm charge length.



CONCLUSION

We have applied the transition state theory to construct a reaction model for the simulation of shock-induced chemical reaction in high explosives. The presence of a characteristic time that governs the fast reaction portion is attributed to the excitation process in producing a thermal nonequilibrium energetic state, which itself is quasi-steady. The energetic state is believed to be electronically excited, and in turn it changes the vibrational mode. Evidence of electronic excitation is found in the optical enhancement of shock to detonation. A separate quantum-mechanical study concludes that there is a characteristic time representing phonon-to-vibron energy transfer that is a form of excitation. This time is almost a constant. At this juncture, we believe we have established a connection between phenomenological modeling using the nonequilibrium concept and the more fundamental quantum-mechanical result; the clue is the constancy of a characteristic time in the reaction process of detonation. From the modeling point of view, the notion of constructing a single rate expression, no matter how sophisticated it may be, becomes less likely. The complexity in physics and chemistry does not render easy formulation. After all, there is no great advantage in numerical computation using a single expression which can be quite complicated. Finally, the interface velocimetry experiment is quite useful to study reaction kinetics in an indirect way, but better time resolution is needed to improve the quantitative aspect in modeling.

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