

EVIDENCE FOR THERMAL EQUILIBRIUM IN THE DETONATION OF HMX

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The validity of modeling the chemical energy release in a detonation with the traditional canonical rate constant depends upon the condition of thermal equilibrium within the reaction zone. In this paper we show that ignition data on HMX from thermal explosion to detonation are all consistent with a single Arrhenius rate constant for chemical energy release. We argue that the model independent existence of a single rate limiting process coupling detonation to thermal explosion is evidence that chemistry in the detonation reaction zone proceeds under conditions of thermal equilibrium in HMX.

INTRODUCTION

The field of detonation physics and chemistry dates back to the first observations of detonation waves by Berthelot and Vielle, and Mallard and Le Chatelier¹ two hundred and twenty years ago. Although a mature field, particularly as regards detonation in gaseous mixtures, issues central to the phenomenon remain unresolved. In particular, considerable effort has been devoted recently to resolving a question fundamental to the understanding of detonation in heterogeneous, solid systems. Does the release of chemical energy in the detonation reaction zone proceed under conditions of thermal equilibrium? This question is crucial to how one considers using rate constant data, when available, to model the detonation front. Under conditions of thermal equilibrium one may predict from a measured canonical rate constant the dependence of energy release rate on

temperature. One can investigate diffraction, corner turning behavior and detonation failure due to dissipative effects. One can incorporate pressure into the known equilibrium free energy expression for the rate constant and investigate the whole suite of detonation phenomena from first principles.

In this letter we present a compilation of ignition data for the energetic nitramine HMX² which shows that the rate of chemical energy release from conditions of thermal explosion to detonation is controlled by a single temperature dependent rate constant. We will further argue that the simplest explanation for this observation is energy release under conditions of thermal equilibrium in this material.

It has been shown³ that even given dephasing times on the order of ps, vibrational equilibration can take up to 10 ns subsequent to a few GPa shock in

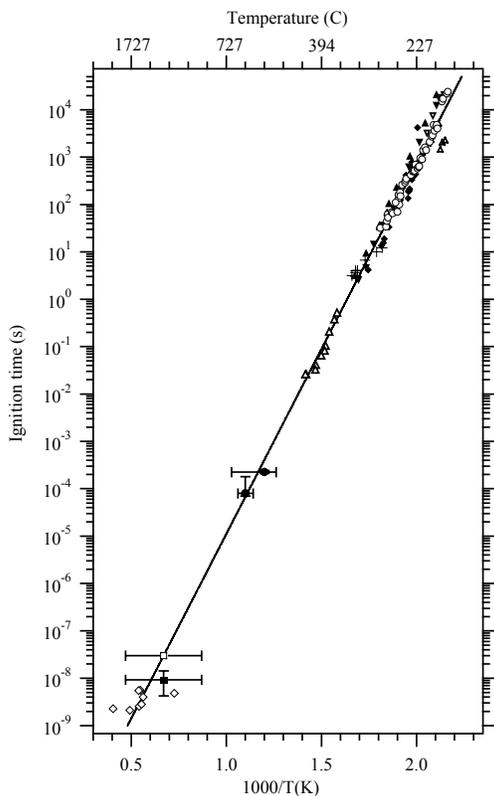


FIGURE 1. IGNITION DATA FROM HMX COMPILED AS DESCRIBED IN THE TEXT.

light diatomic molecules. More recently the argument for detonation controlled by nonequilibrium conditions in large polyatomic systems was made in a very elegant series of experiments by Tas *et al.*⁴ where they have shown that shock pressurization and heating in polycrystalline anthracene proceeds on a time scale of <25 ps. Anthracene, a tricyclic, aromatic hydrocarbon molecule, also figured significantly in the experiments of Lambert *et al.* in the mid eighties⁵ designed to address another fundamental question in chemical physics at that time, the timescale for internal vibrational energy redistribution (IVR). In these experiments it was shown that the redistribution of vibrational energy, deposited coherently into a manifold of

energy levels on the first excited singlet electronic surface, proceeded on a timescale of 10 ns, and was characterized by regimes passing from discrete exchange of energy between modes to exponential dissipation into the larger manifold of vibrational states, depending on the density of states local to the excitation energy. The assertion by the authors of Ref. [4], that the timescale of shock heating of the intermolecular manifold of phonon states was sufficiently fast to enable nonequilibrium distributions of vibrational energy to arise, particularly as energy is coupled into the intramolecular vibrational modes,⁶ is thus consistent with the known dynamics of vibrational redistribution in this system. One beginning of an answer to the question of equilibrium in the reaction zone of a solid energetic system, also composed typically of large polyatomic organic species, thus seems to be that heating can proceed fast enough to generate nonequilibrium conditions which could persist for times comparable to the reaction zone time. The supposition that nonequilibrium conditions may obtain in detonation has resulted in a number of calculations concerning the possible ramifications for the chemistry of energy release.^{6,7}

However, the fact that reaction zone heating proceeds on the timescale of mechanisms of equilibration does not of course preclude equilibration among modes constituting dominant reaction coordinates in any given system. In this paper we show that the time to ignition as a function of temperature in HMX throughout the full range of energetic response is consistently represented by a single, first order, temperature dependent chemical rate constant. This evidence does not depend on the details of the

chemical decomposition model. Here we gather data in support of this assertion from experiments under conditions ranging from thermal explosion⁸⁻¹¹ and fast pyrolysis¹² to laser ignition¹³ and impact induced shear¹⁴ and frictional heating.¹⁴ Most importantly, we reinterpret a classic set of detonation initiation experiments¹⁵ where the heating profile from the confined surface of an HMX plastic bonded explosive was measured radiometrically subsequent to shock passage. We extract an experimentally constrained chemical rate constant for energy release from these experiments that is consistent with the other suite of thermally induced explosion experiments. Finally, we show by one dimensional ZND detonation calculations that the single rate constant so determined is also consistent with a measured property of the stable detonation wave in HMX, the duration of the reaction zone.^{16,17}

COMPILATION OF THERMAL IGNITION DATA FOR HMX

The set of ignition data for HMX based samples is shown in Figure 1. The data are compiled, with the exception of the detonation data, as the measured time to ignition as a function of the inverse of the applied temperature. In all cases except reaction zone measurements the temperature applied to the sample was reported. The data set is to our knowledge inclusive, with the following exceptions. Some unconfined thermal explosion experiments have been neglected from the data set as the loss of reactant gases on long timescales can lead to spuriously long ignition times and even ignition in the gas phase away from the sample. In the fast pyrolysis data set

of Brill and Brush¹² on thin films, we have shown only the subset of data where reaction time was attributed to chemistry rather than thermal transport. We have not included data obtained from experiments under conditions of high quasistatic pressurization. The reasons for this exclusion are discussed below.

The data of Figure 1 from confined thermal explosion studies are plotted as filled diamonds,⁸ filled triangles and inverted triangles,⁹ open triangles and inverted triangles,¹⁰ and open circles.¹¹ The data from fast pyrolysis studies are plotted as crosses.¹² The laser ignition data are plotted as open triangles.¹³ The shear and frictional heating data are plotted as filled circles.¹⁴

DETONATION DATA: INITIATION

The ignition time and temperature are not directly reported in the detonation initiation data of Ref. [15]. In these experiments a weak shock, on the order of 2 GPa, was launched through a thin sample of an HMX plastic bonded explosive, PBX 9404¹⁸ by projectile impact. Subsequent to shock passage through the sample, radiometric measurements were made from the sample surface from which a sample surface temperature was deduced. The general observation in a number of experiments was a linear temperature rise in the sample following shock passage, from ambient initial temperature to approximately 1800 to 2300 K. The temperature then fell abruptly upon ignition and disassembly of the sample apparatus. The time to the temperature peak varied from 6 to 10 μs , and corresponded well to known detonation initiation times in PBX 9404 measured as

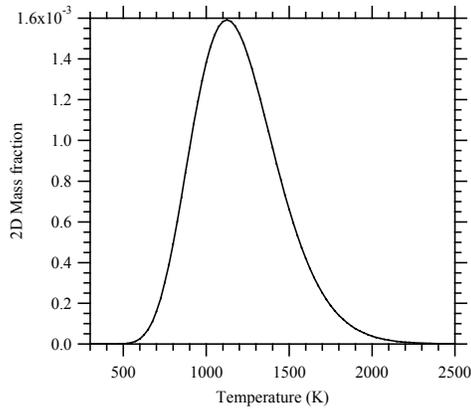


FIGURE 2. TWO DIMENSIONAL TEMPERATURE DISTRIBUTION PERPENDICULAR TO THE DIRECTION OF THE SHOCK CALCULATED FOR A PARTICLE VELOCITY OF 3000 M/S, AND AN ASSUMED MEAN TEMPERATURE OF 1500 K.

a function of impact pressure. The main point in the interpretation of these data by the authors was the observation of heating by hot spot formation in the material, and the separation of shock induced heating (i.e. mechanical heating) from ignition (i.e. heat released through chemical decomposition) as indicated by hydrodynamic calculations.¹⁹ The authors also noted that this separation was consistent with earlier observations.²⁰

We perform a somewhat different analysis of the data in order to directly extract the dominant chemical rate constant. In this analysis one assumes the measurement of temperature in these experiments to reflect the true bulk heating of the sample by conduction from the initial, local regions of shock induced heating. This assumption is valid in these experiments due to the large integration area (2 mm x 2 mm) of the radiometric measurement relative to the assumed area

of an initial hot spot, ($\sim 1 \mu\text{m}$), and the uncertainty concerning the density of hot spots. Under such conditions of equilibrium heating, a result from the kinetics of combustion allows the direct determination of the dominant rate of chemical decomposition leading to ignition.²¹ Ignition in an explosive system subject to a linear heating profile occurs when the heat generated by chemical decomposition approximately equals the applied heating rate,

$$-\frac{\partial\left(\frac{1}{k}\right)}{\partial T} = \frac{\Delta t}{\Delta T} \quad (1)$$

where k is a first order Arrhenius rate constant, $1/k$ is a characteristic reaction time, t is the time and T the temperature. This can be integrated at the ignition temperature, T_i , to yield the order of magnitude estimate

$$\frac{1}{k(T_i)} \cong o \frac{\Delta t}{\Delta T} \quad (2)$$

where o is a constant of order unity in units of temperature. We have thus plotted the data of Ref. [15] as the inverse of the observed linear heating rate against the inverse of the observed peak temperature in Figure 1 (open diamonds).

DETONATION DATA: STABLE DETONATION

Finally, we show that this rate constant is also consistent with the stable detonation wave in HMX. Davis has developed and calibrated a complete equation of state (EOS) for an unreacted explosive, $E = E(S, v)$, where E is the

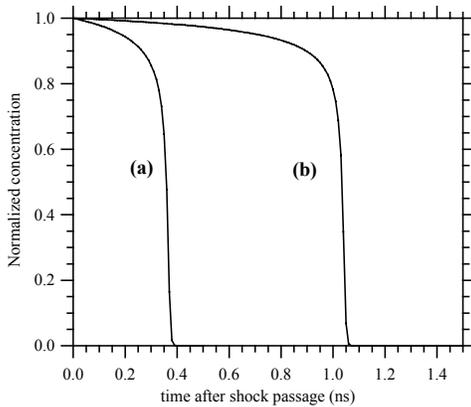


FIGURE 3. PROGRESS VARIABLE AS A FUNCTION OF TIME USING THE RATE CONSTANT DETERMINED IN THIS WORK.

energy, v the volume and S the entropy.²² The EOS was calibrated by Davis²² using low pressure shock data,^{18,23} and steady state detonation measurements.¹⁶ From this EOS an expression relating temperature at the shock front to particle velocity at the shock front can be derived,

$$T = T_o \left(1 + \frac{U_p^2 (1 + \alpha)}{2 C_v T_o} \right)^{\frac{1}{1 + \alpha}} \quad (4)$$

where T is the temperature, T_o is the reference temperature (298 K), U_p is the particle velocity, C_v is the constant volume heat capacity, and α is a calibration constant. This equation provides an estimate of the bulk temperature as a function of particle velocity. However, the temperature distribution in a shocked explosive is extremely non-uniform, with significant local variations in temperature. The distribution of temperatures at the shock front will strongly influence the effective volumetric reaction rate. Relatively simple calculations of temperature

distributions in shocked PBX 9501 show that the distribution can be approximated by a gamma function, whose mean is represented by the bulk temperature.²⁴ Davis has reported some representative values for assumed temperatures ranging from 1500 K to 1900 K at the von Neumann spike. We find that using Davis' value of α corresponding to the lowest temperature, 1500 K, and the rate constant determined above give a reaction rate consistent with measured reaction zone thickness for detonating PBX 9501.^{16,17}

The calculated temperature distribution in the unreacted material at the detonation state is shown in Figure 2. In Figure 3, we show the extent of reaction as a function of time subsequent to shock passage, for (a) using the temperature distribution of Figure 2,²⁴ and (b) using a temperature of 1500 K. Finally, we have plotted the reaction zone time of Ref. [16] in Figure 1 (open square) as a function of temperature using 1500 K, with error bounds from the distribution of Figure 2. We have also plotted older reaction zone measurements¹⁷ (solid square) in Figure 1 using the same criterion for temperature. We stress that we do not claim we have used these kinetics to derive a predictive initiation model, however, we believe the results show the kinetics to be consistent with the detonation behavior of PBX 9501. The derivation of such chemical initiation models based on these observations is underway in our laboratory.²⁵

THE LIMITING CANONICAL RATE CONSTANT FOR HMX

We fit the ignition data set of Figure 1 using the classic Arrhenius form for the temperature dependence of the canonical rate constant $k = A \exp(-E/RT)$, where k is a first order rate constant, A a prefactor, E the activation energy, R the gas constant and T the temperature. We assume the measured ignition times compiled in Figure 1 to reflect a characteristic reaction time to ignition of $t = 1/k$, which is equivalent to assuming a first order rate law with ignition at a fractional decomposition of $1/e$. The solid line of Figure 1 is the result of a linear regression of the data set according to

$$\ln(t) = \left(\frac{E}{R}\right) \frac{1}{T} - \ln(A) \quad (3)$$

which yields values of $E=149 \pm 1.1$ kJ/mole and $A=e^{29.35 \pm 0.26} \text{ s}^{-1}$.

THE ROLE OF PRESSURE

The extension of a single rate limiting step to the detonation regime brings up an obvious question. Where is the pressure dependence to this line? While experiments done under static pressurization have not been included in the data set collected here, experiments which achieve heating in shear,¹⁴ impact to initiation¹⁵ and detonation^{16,17} involve very high dynamic rates of pressurization. The pressure dependence one expects is a function of the reaction mechanism. If the rate limiting component of the mechanism is in the solid state and has a positive volume of activation, pressure will slow the reaction. If the rate limiting mechanism occurs in the gas phase, an increase in pressure will typically increase the reaction rate. If the rate limiting component involves sublimation, it will

be relatively insensitive to applied pressure. For instance, to increase the sublimation rate by tenfold would require pressures on the order of tens of gigapascal, on the order of the CJ pressure for HMX. The experimental observation that the measured ignition times do not show a pressure dependence is therefore at worst ambiguous with respect to the chemical mechanism, and at best can be used as a clue towards the rate limiting reaction mechanism.

Finally, the linearity in this data set is achieved by the exclusion of experiments done at high static pressure, which have resulted in a number of rate constant determinations which are not consistent with the single rate constant presented here.²⁶ Two possibilities must be considered: 1) The extrapolation of these data into the high pressure regime¹⁴⁻¹⁷ is incorrect or 2) The application of static high pressure is not equivalent to the dynamic pressurization experienced in these experiments. There is little interpretation required to plot the faster rate data. The inclusion of dynamic data and the exclusion of static data is a natural separation that we have not created, only observed. The data themselves indicate different behavior in these two regimes. We are therefore left with option two. In the absence of a detailed model of pressurization in heterogeneous material we can only speculate as to why pressure is not asserting a greater influence on the rate data. Such speculation here takes two forms. In the first place it is very likely that the rate limiting component of the global mechanism under discussion here does reflect a chemical or physical process relatively insensitive to pressure. As previously discussed such robust processes as sublimation satisfy this

criteria. In the second place pressurization in a heterogeneous solid is a quite complex process. For example pressures greater than the elastic limit cannot be sustained by the solid until internal void space has been removed and a fully dense state is achieved. The time scale for this is likely a function of material flow at the particle velocity behind the shock and the mean length scale of the internal structure. For 2000 m/s and 2 μm this time is 1 ns. In other words for the first 10% of the measured reaction zone time pressures are rising in concert with temperature and chemical evolution. In this light it is perhaps not surprising that the data necessitate a more sophisticated consideration of the role of pressure, even in detonation.

CONCLUSION

The linear relationship describing the ignition data shown in Figure 1 is the central result of this paper. The use of ignition data, particularly the time to ignition as a function of an applied thermal boundary condition, to constrain chemical mechanism dates back to papers by Zel'dovich.²⁷ We take the successful representation of HMX ignition data by a single rate constant to indicate a common rate limiting reaction step in the decomposition of HMX operative throughout the range of energetic response in this system. The existence of a common rate limiting chemistry for ignition and detonation in this material couples two fields of energetic response that have previously been considered separate. Further, a measured canonical rate constant $k(T)$ is in fact an ensemble measurement of the rate constant as a function of the energy of the system,

$$k(T) = \int_{E_0}^{\infty} P(E, T) k(E) dE \quad (5)$$

where $k(E)$ is the rate constant as a function of energy along the reaction coordinate, E_0 is the activation energy for passage along the coordinate and $P(E, T)$ the distribution of energy in the system as a function of temperature. The exponential dependence on temperature derives from the thermal averaging of energy among the vibrational degrees of freedom in the molecule. Linking the dominant rate constant in detonation with that measured for other regimes where thermal equilibrium is guaranteed is thus a strong inference that the chemistry of detonation in this system is the same chemistry (at least in the rate limiting step) and proceeds under the same condition of equilibrium

We thus conclude that while it has been shown that shock heating proceeds fast enough to generate initial nonequilibrium energy distributions, in HMX the rate of energy release in the detonation reaction zone is consistent with the same chemical rates that dominate under conditions that are characterized by thermal equilibrium.

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