

A Unifying Thermodynamic Model for the Rate of Energy Release in the Reaction Zone of Solid Secondary Explosives

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1 Introduction

The difficulties of extrapolating temperature dependent chemical rate constants obtained by measurements of thermal decomposition or ignition under non-shock conditions to the detonation regime are well known. In the case of the detonation chemistry of solid explosives the most famous example is perhaps that provided in the review of the physics of detonation by Eyring for the case of lead azide.¹ In this case of an example primary explosive he showed that a plot of the logarithm of the measured ignition time as a function of the inverse temperature showed two distinct linear regimes, indicating two dominant rate constants, each limiting rate over a different range in temperature. Eyring goes on to argue that it is very unlikely that a similar mechanism of energy release would be operable over the ranges of temperature, and particularly rate, that span the 1000 to 2000 C range in temperature separating thermal decomposition by direct heating and detonation.

While this has been accepted wisdom for half a century, and likely most generally true, we have previously presented evidence of a single mechanism limiting chemical energy release for an important secondary explosive, HMX, for which ignition data are available over a wide range of temperature. We provide this evidence in a similar manner, as an Arrhenius plot of the logarithm of the time to ignition as a function of the inverse boundary temperature for temperatures spanning the full range of response for this molecule, from the minimum thermal ignition temperature to detonation.² Furthermore, we have provided a mechanistic understanding for the slope of the line fitting these data, and therefore a model for the activation energy of the chemical process limiting rate and energy release in the solid decomposition of this molecule. Rather than the typical association of this activation energy with that activating the breaking of a covalent bond, as assumed in Eyring's discussion above, we show that the activation energy measured for the suite of ignition data for HMX can be determined as a function of the condensed phase thermodynamics of the molecule, specifically the bulk phase free energies of sublimation and vaporization. Models of complex thermal decomposition and ignition have incorporated this model into larger mechanisms of solid and gas phase decomposition,³ as well as a model of steady detonation.^{4,5}

In this publication we present an important extension of these ideas to other molecules of the class of solid secondary explosives. The thermodynamic nature of the model for the single rate dependence

governing thermal response in this example allows for a reduced representation of the rate constant as a universal function of the sublimation and vaporization free energies. This allows direct comparison of ignition data for a host of molecules for which data are available over a more limited range than are available for HMX. We have previously shown a similar reduced representation of thermal decomposition data for secondary explosives exhibiting the phenomena of melt acceleration, an increase in decomposition rate as the melting point is approached.⁶ In this paper we will show comparisons for data from HMX, TATB and PETN.

2 Thermal ignition data for HMX, TATB and PETN

We show a collection of thermal ignition data for three important solid secondary explosives TATB, HMX and PETN in Fig. 1. The data are plotted as the time to ignition ($\ln$ plot) as a function of the inverse temperature. The data are selected from experiments which meet three important criteria, that the highest boundary temperature is located and directly measured, that the experiment is confined such that decomposition gasses are not released, either as an encased experiment or by inertia at sufficiently high rates of heating, and that the sample is not prepressurized, as in a high pressure cell. The data are all referenced in the figure caption. For each molecule the single linear behavior is apparent, and independent determinations of these slopes will be discussed in the next section.

3 A thermodynamic model of the ignition slope

The slopes of the ignition lines of Fig. 1 can be calculated as the geometric mean of rate constants thermally activated by the free energies of sublimation and vaporization as

$$t = \frac{1}{\sqrt{\nu k_{sub} k_{vap}}}, \quad (1)$$

where the form of the rate constant is given by the traditional Arrhenius equation

$$k_i = \nu \exp\left(-\frac{\Delta G_i}{RT}\right) \quad (2)$$

and i denotes either sublimation (sub) or vaporization (vap). The constant ν is fit to the data, and is the only fitting constant for each molecule.

A dimensionless version of Eq. (1) can be obtained by creating the dimensionless temperature $\ln(a) = -(\Delta G_{sub} - \Delta G_{vap})/RT$. If we take advantage of the fact that $\Delta G_{sub} - \Delta G_{vap} = \Delta G_{fus} = \Delta H_{fus} - T\Delta S_{fus}$, $\Delta H_{fus}/\Delta S_{fus} = T_m$, and $T \sim T_m$ near the melting point

$$a = \exp\left(-\frac{\Delta H_{fus}}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right) \quad (3)$$

We compile the thermodynamic parameters in Table I. We can express Eq. (1) in dimensionless form as.

$$\nu k_{sub} t = \sqrt{a}. \quad (4)$$

This dimensionless comparison for TATB, HMX and PETN are shown in Fig. 2.

4 Discussion and Conclusions

The fact of a single mechanistic description of chemical decomposition for HMX is a fact of the data set of Fig.1, and the single slope description of the time to ignition as a function of temperature. The association of the overall activation energy defining this slope with the geometric mean of rate constants constructed from free energies of activation describing the thermodynamic state of the bulk crystalline phase is a mathematical construction. We are pursuing a molecular description of the mechanism of decomposition that this construction reflects and that will be the focus of future publications. The normalization of Eq. (1) to the universal description in Eq. (4) is also a construction, but we believe this normalization of the free energies of sublimation and vaporization to be a significant clue to the underlying mechanism.

The ability now to predict the governing rate constant for a number of secondary explosives will enable new research into temperature dependent models of reactive burning in solid secondary explosives.

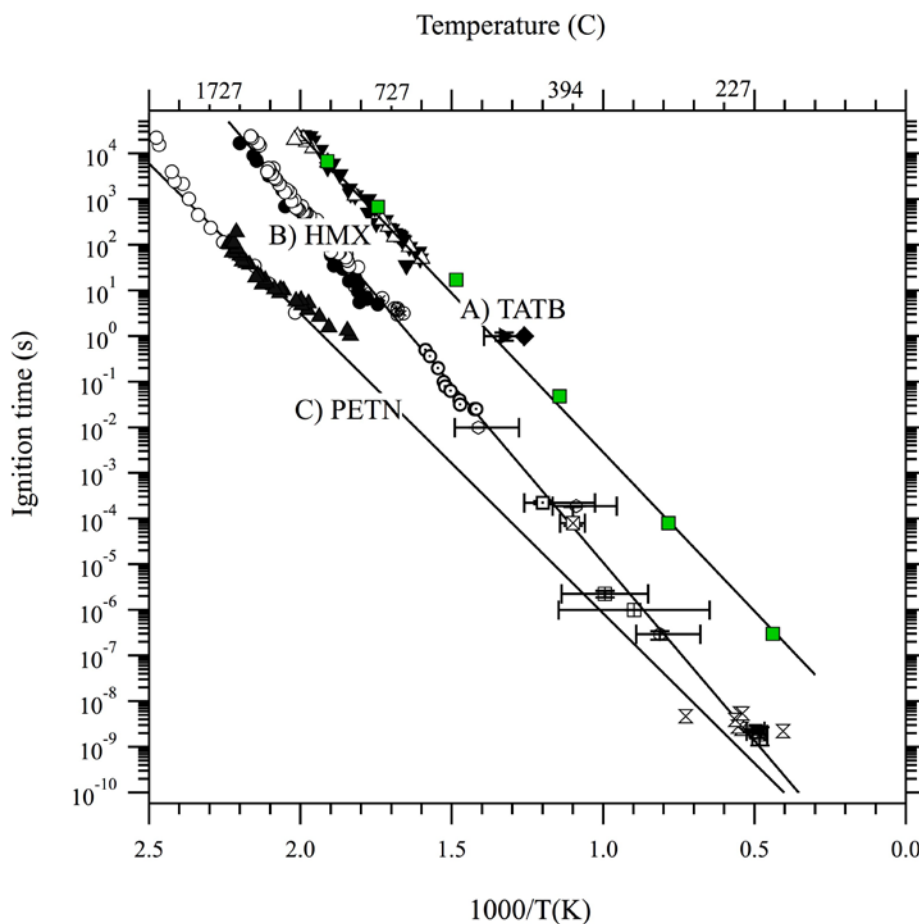


Figure 1. A.) Ignition data from a number of different experiments in this and other laboratories plotted as the ignition time as a function of the inverse temperature. Thermal explosion data, plotted as the ignition time as a function of the inverse boundary temperature are shown as the open⁷ and filled⁸ circles. Laser induced temperature jump,⁹ circles with an included x and laser ignition data,¹⁰ circles with an included dot, are plotted as the ignition time as a function of the inverse of the directly measured surface temperature. Ignition induced by fast friction, and shear, Square with an included dot,¹¹ are plotted as the ignition time as a function of the inverse of the directly measured surface temperature. Ignition induced by fast compression and flow under isothermal heating conditions, blue squares with an included cross,¹² are plotted as the ignition time as a function of the inverse of the directly measured surface temperature. Ignition induced by fast compression and flow under linear heating conditions, blue squares with an included x,¹² are plotted as the inverse of the linear heating rate as a function of the peak temperature at ignition. Laser assisted ignition temperatures¹³ presented here are plotted as the ignition time as a function of the isothermal temperature, and as the inverse heating rate as a function of the maximum observed temperature at ignition, hexagon with an included dot. Data from run to detonation experiments are also plotted as the inverse heating rate as a function of the maximum observed temperature at ignition, open double triangle¹⁴. The green squares are computational results to be described below. B) Thermal explosion data for TATB based explosive formulations, plotted as the ignition time as a function of the inverse boundary temperature are shown as the open⁷ and filled⁸ triangles. Combustion data are shown as the filled diamond.¹⁵ The large squares (green online) are calculations to be described later. C) Thermal explosion data for PETN based explosive formulations, plotted as the ignition time as a function of the inverse boundary temperature are shown.^{16, 17}

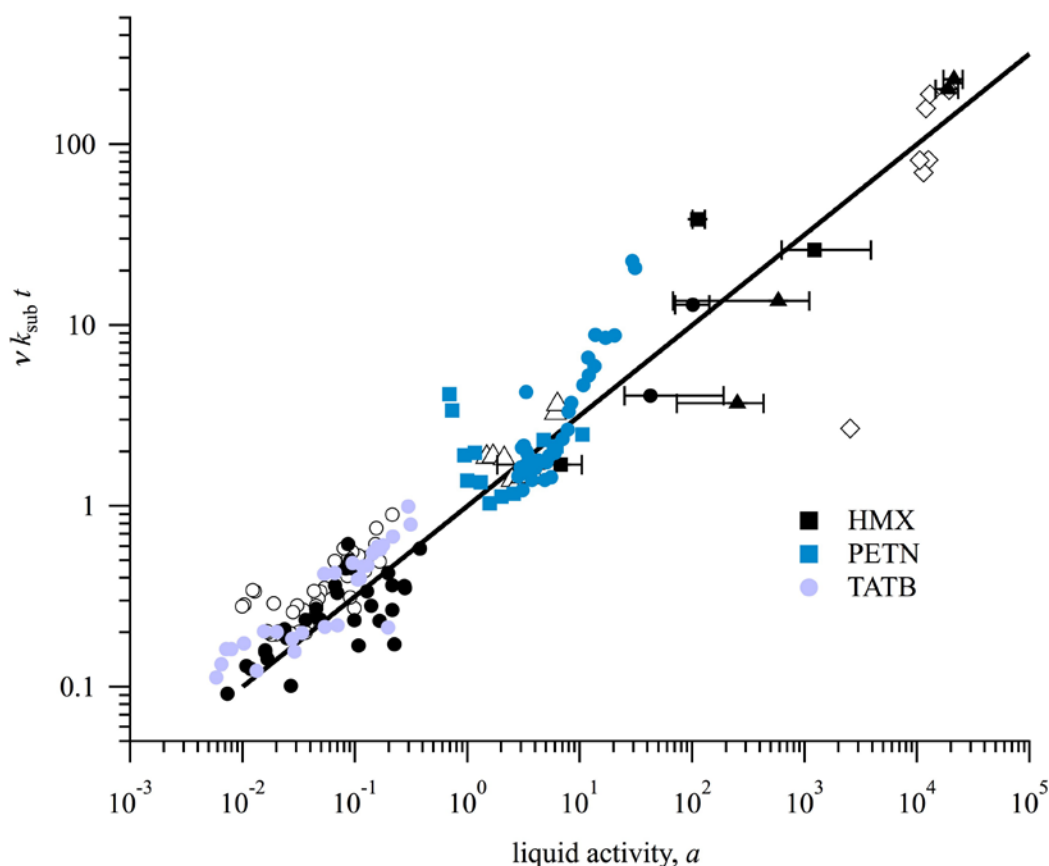


Figure 2. Ignition data of Fig. 1 normalized to the dimensionless time and normalized thermodynamic activity a as discussed for Eq. (4)

Table 1: Thermodynamic and kinetic parameters. Units of enthalpy are kJ/mole. Units of temperature are K.

Explosive	ΔH_{fus}	T_{m}	ν
HMX	69.900 ¹⁸	278 ¹⁸	0.085
DATB	35.250 ¹⁹	294 ²⁰	1.800
PETN	49.338 ²¹	141 ²⁰	1.000

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