Application of Solid-Phase Transition Kinetics to the Properties of HMX

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Introduction

THE chemical HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) is an important nitramine monopropellant. Recently we have determined the pressure-temperature phase diagram for the conversion of the β polymorph to the δ polymorph.[1,2] This phase transformation involves both a major disruption of the crystal lattice from the monoclinic to the hexagonal crystal system[3,4] and a ring conformation change of β (chair) to δ (chair-chair) shown in Fig. 1.

The volume expansion associated with the first-order $\beta \rightarrow \delta$ phase transition (the density is 1.90 g/cm^3 for β and 1.78 g/cm^3 for δ) will lead to strain and microfracturing in the crystallites. Hence, the mechanical properties and combustion characteristics of HMX could be affected by this transition. The phase transformation temperature depends on the applied pressure[1,2,5] and the particle size of HMX.[1,2] At very high pressures where the temperature of the phase transition is high enough to produce considerable decomposition, the enthalpy change ΔH for the conversion is similar to the activation energy of decomposition.[5] Hence, at high pressure, the $\beta \rightarrow \delta$ transformation could be a source of fracturing and heat release in the thermal wave below a burning surface. Such events concern deflagration-to-detonation transitions and combustion modeling of HMX, particularly with larger particle sizes.

Intimately coupled to the thermochemical analysis of the $\beta \rightarrow \delta$ transition is the kinetics of the process. While a number of thermochemical studies are now available,[1,2,6,7] no kinetic data on this phase transition have been obtained. This void is undoubtedly due to the difficulty of measuring the rates of solid-solid transitions.[8] In fact, the entire domain of first-order solid-solid phase transitions in organic materials at elevated temperatures is virgin territory. We have determined the Arrhenius parameters by using Fourier transform/infrared (FT-IR) spectroscopy. Full reports describing the methodology of phase transition kinetics studies by FT-IR and the kinetic stabilities, applications, and significance of other HMX polymorphs appear elsewhere.[9,10] This Note deals with the relationship of the $\beta \rightarrow \delta$-HMX solid-phase transition kinetics to propellants.

Experimental

A sample cell specially designed for the particular requirements of this work was constructed. Nominal 8 μm HMX was dusted between two NaCl plates which in turn fit snugly into an aluminum block. The block could be heated and the temperature regulated with considerable precision. However, it was discovered that a drop of silicone fluid on the plates greatly improved the heat transfer to the HMX crystals. The temperature was measured with a digital thermometer. The infrared spectra were recorded on a Nicolet 7199 FT-IR employing an MCT detector.

In a typical experiment, the sample was heated at a rate of approximately 2°C/min to the desired temperature in the range of 165-194°C. The temperature was quickly stabilized to ± 0.2°C and four interferograms were coadded. The loss of intensity of the 958 cm^{-1} mode due to C-N stretching in β-HMX was monitored isothermally as a function of time. This mode is reasonably well separated from δ-HMX bands which grow in place of the β-HMX bands. The absorbance of the 958 cm^{-1} band is proportional to the concentration of β-HMX according to the Beer-Lambert law. This procedure was repeated at a number of temperatures using a fresh sample for each run.

In order to be certain that the loss of intensity in the 958 cm^{-1} band did not arise from decomposition or sublimation of the sample, the spectra were routinely inspected to insure that δ-HMX bands grew concomitantly with the loss of β-HMX bands. Confinement of the sample between the NaCl plates and the presence of the silicone fluid precludes significant sublimation from occurring.

Results and Discussion

ΔH for the $\beta \rightarrow \delta$-HMX transformation at pressures below 138 MPa (20,000 psi) is small and endothermic (10-20 kJ/mole),[1,2,6,7] but becomes competitive with the activation energy for decomposition at higher pressures.[2] At propellant combustion pressures, the phase transition contributes little to the overall energy balance. However, because volume expansion occurs, it could be an important factor in the development of cracks and strains below the surface of a decomposing crystallite. Fracturing, perhaps resulting from these strains, is observed during the combustion of crystals of HMX.[11-13]

While the fine points of solid-phase transition kinetics involve factors such as nucleation of the new phase, growth of the boundary, and lattice imperfections,[14] the experimental methods used to diagnose complex systems do not provide sufficient detail to warrant a comprehensive exposition. First-order kinetics was observed here for the $\beta \rightarrow \delta$ transformation of HMX within the limits of the measurement. Plots of $\ln$ (concentration) vs time yielded straight lines. An experimental Arrhenius plot for the $\beta \rightarrow \delta$ transition is shown in Fig. 2. The Arrhenius equation (1) was obtained.

$$k = 7.9 \times 10^{19} e^{-48800/RT}, \ \mathrm{s}^{-1} \qquad (1)$$

The pre-exponential for this solid-phase reaction probably involves an inseparable combination of nucleation and propagation processes. On the other hand, the activation energy E_a of 204 ± 14 kJ (48.8 ± 3.3 kcal) has important implications with regard to the material properties of HMX.

The large value of E_a for the $\beta \rightarrow \delta$ polymorph conversion results from the high stability of the HMX crystal lattice. The electrostatic interactions afforded by the ribbon of alternating positive and negative charged atoms[15] produce a formidable potential energy barrier to a disruptive phase transition. It is

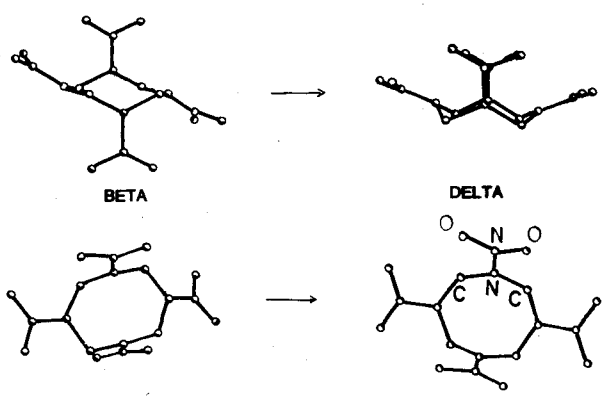

Fig. 1 The molecular conformation change during the $\beta \rightarrow \delta$-HMX solid-phase transition.

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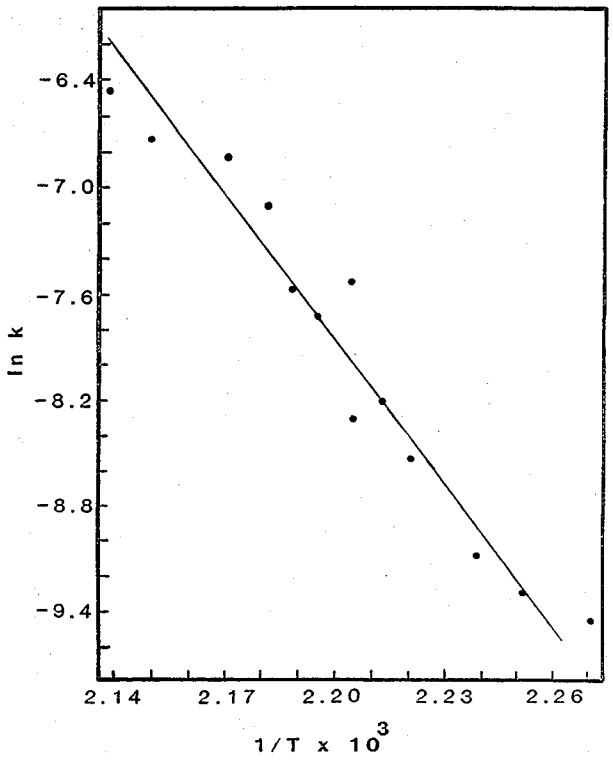

Fig. 2 The Arrhenius plot for the $\beta \rightarrow \delta$-HMX solid-phase transformation (correlation coefficient is 0.975).

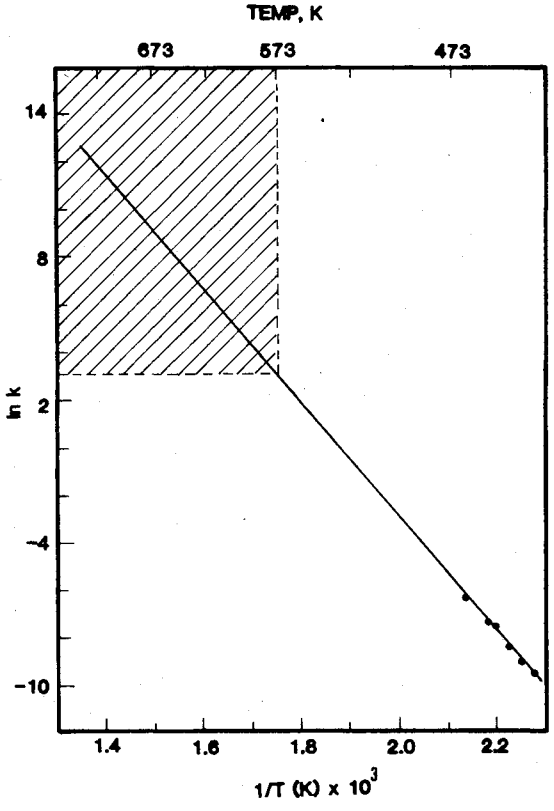

Fig. 3 Extrapolation of the Arrhenius data for the $\beta \rightarrow \delta$ phase transition from the measured range into the temperature region typical of a burning propellant surface.

instructive to note that the chair conformation of β-HMX can be converted to the chair-chair conformation of δ-HMX by a simple ring-puckering vibration. Vibrations of this type typically have low potential energy barriers. Consequently, for all practical purposes, E_a for the phase transition represents the barrier to disruption of the numerous intermolecular forces in the HMX crystal lattice.

We and others have found that impurities and the past treatment of the sample can alter the temperature of the phase transition. A solid-solid transition having a structural change and a large E_a will be subject to significant alterations by crystal imperfections.

The high value of E_a is consistent with the fact that HMX decomposes without undergoing an authentic melting step. Vigorous chemical decomposition occurs during liquefaction. It is remarkable that Eq. (1) is very similar to Arrhenius equations obtained for the decomposition of HMX in the condensed phase.[16,17] The similarity of the Arrhenius data for the $\beta \rightarrow \delta$ phase transition and the condensed-phase decomposition of HMX suggests that the same processes may be rate determining in these different events. It is the disruption of the intermolecular forces that leads to the solid-solid phase transition. This same phenomenon may be what has been measured by kinetics during the decomposition of HMX in the condensed phase. This contrasts with all previous interpretations of decomposition kinetics which assume covalent bond breaking steps are rate determining.

Over the temperature range which the $\beta \rightarrow \delta$ transformation is of interest (160-400°C), E_a should be relatively independent of temperature.[18] This being the case, the large value of E_a causes the reaction rate to increase rapidly with increasing temperature. Linear extrapolation of the rate of the $\beta \rightarrow \delta$-HMX transition to the temperature range of the burning propellant surface indicates a very fast rate of conversion (Fig. 3). The rate is much faster than the regression rate of the thermal wave. Therefore, the thermochemical and kinetics measurements point to the $\beta \rightarrow \delta$ phase transition in the HMX crystallites as the first chemical change when the nitramine is heated. The rate-determining step in decomposition appears to involve primarily the breakdown of the intermolecular forces between species (HMX molecules and decomposition products) in the solid and liquid phases.

Acknowledgment

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Vibrations of Nonuniform Beams with One End Elastically Restrained against Rotation

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Introduction

THIS Note deals with the determination of the fundamental frequency of the transverse vibration of nonuniform beams with one end elastically restrained against rotation and carrying a mass M at the free end. It is also assumed that the structure is subjected to an axial force F, see Fig. 1.

The analysis is developed by means of the Ritz method on the basis of classical beam theory. Two situations are considered: 1) a linearly tapered beam (Fig. 1a), and 2) discontinuous variation of the cross-sectional area and moment of inertia of the structural element (Fig. 1b).

A review of the recent technical literature reveals that these two cases have not been extensively studied.[1-3] No claim of originality is made, but it is hoped that design engineers will find the present approach and results useful in their work.

Analysis of the Problem

Linearly Tapered Structural Element

The thickness h and the width b at a position x along the linearly tapered beam as shown in Fig. 1a are given by the expressions,

$$h=(h_1-h_0)\bar{x}+h_0, \qquad b=(b_1-b_0)\bar{x}+b_0$$

Then, the cross-sectional area A and the moment of inertia I result in

$$A=A_0(\delta\bar{x}+1)(\gamma\bar{x}+1), \qquad I=I_0(\gamma\bar{x}+1)(\delta\bar{x}+1)^3$$

where

$$\bar{x}=x/L,\ \gamma=\alpha-1,\ \delta=\beta-1,\ A_0=b_0h_0,\ \text{and}\ I_0=b_0h_0^3/12$$

with

$$\alpha=b_1/b_0 \ \text{and}\ \beta=h_1/h_0$$

(width and thickness ratio, respectively).

In order to obtain an approximate solution by the Ritz method one minimizes the functional, $J[W]=U_{\max}-T_{\max}$ with respect to the arbitrary constants contained in the approximating function ($U_{\max}$ = maximum strain energy, $T_{\max}$ = maximum kinetic energy).

When determining the fundamental mode of vibration, it is convenient to use the approximation[4]

$$W(x)\simeq W_a(x)=C_0(\alpha_{40}\bar{x}^4+\alpha_{30}\bar{x}^3+\alpha_{20}\bar{x}^2+\alpha_{10}\bar{x}+\alpha_{00})$$
$$+C_1(\alpha_{41}\bar{x}^5+\alpha_{31}\bar{x}^4+\alpha_{21}\bar{x}^3+\alpha_{11}\bar{x}^2+\alpha_{01}\bar{x}) \qquad (1)$$

which satisfies the boundary conditions,

$$W(1)=0 \qquad (2a)$$

$$\frac{dW}{d\bar{x}}\bigg|_{\bar{x}=1}=-\frac{\phi_1 EI_1}{L}\frac{d^2W}{d\bar{x}^2}\bigg|_{\bar{x}=1} \qquad (2b)$$

$$\frac{d^2W}{d\bar{x}^2}\bigg|_{\bar{x}=0}=0 \qquad (3a)$$

$$\frac{d^3W}{d\bar{x}^3}\bigg|_{\bar{x}=0}=0 \qquad (3b)$$

Equation (3b) does not take into account the existence of the concentrated inertial force. This approximation considerably simplifies all calculations.

Replacing Eq. (1) in the functional and minimizing it with respect to C_0 and C_1 one obtains, from nontriviality considerations, a frequency equation of the type

$$\begin{vmatrix} C_{11}(\omega) & C_{12}(\omega) \\ C_{21}(\omega) & C_{22}(\omega) \end{vmatrix} = 0 \qquad (4)$$

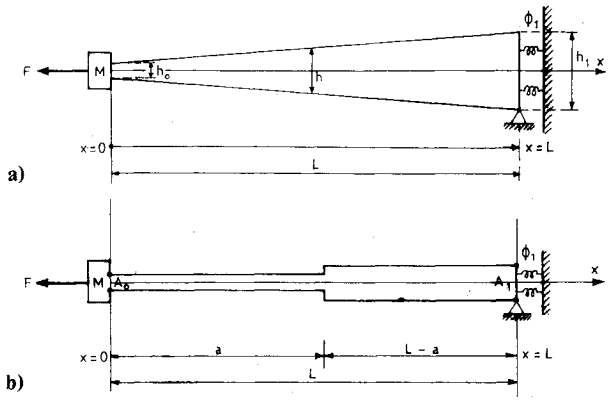

Fig. 1 Vibrating structural elements under study: a) beam with linearly tapered cross section, b) case of discontinuous cross section.

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