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APPLICATION OF ISOTHERMAL CALORIMETRY AND UV
SPECTROSCOPY FOR STABILITY MONITORING OF
PENTAERYTHRITOL TETRANITRATE

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OCT 26 1992**ABSTRACT**

Thermal stabilities for a series of pentaerythritol tetranitrate (PETN) samples with variable surface areas were monitored by isothermal calorimetry and UV spectroscopy over the temperature range of 363 to 408 K. Isothermal induction times measured with constant volume calorimetry under an air atmosphere and NO evolution rates monitored by UV absorbance at 213 nm under vacuum correlated with the PETN surface area at temperatures equal to or exceeding 383 K. Rate data measured at 383 K are in accord with predictions based on detailed kinetic modeling. Below 383 K, NO evolution data suggested that additional geometric factors may be significant in controlling PETN stability. Mechanisms for influencing surface area upon the rate-determining step are addressed.

INTRODUCTION

Advancing applications technology coupled with increased environmental, safety, and health regulations require accurate and precise methods for surveying the stability of energetic materials subjected to long-term aging. These requirements necessitate the need for a more fundamental understanding of the chemistry, in particular the kinetics for degradation, of pentaerythritol tetranitrate (PETN). In previous work, it was demonstrated that an atmosphere of NO₂ above PETN within a closed system reduced the isothermal induction time, as recorded by conventional isothermal calorimetry [1]. These results were shown to be quantitatively in accord with a simple phenomenological model based on a law of autocatalytic rates arising from combined melt-decomposition and secondary chain initiation by NO₂. In this paper, the influence of surface area upon the

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low-temperature aging of PETN and the evolution of NO was investigated by isothermal calorimetry and UV spectroscopy. Rate data are shown to be in accord with detailed kinetic modeling for decomposition of PETN. Specific mechanisms to account for the influence of surface area upon low-temperature degradation of PETN and for the evolution of NO and NO₂ are discussed.

EXPERIMENTAL

Isothermal induction times for PETN samples with surface areas within the range of 3600 to 12000 cm²g⁻¹ were recorded with a Setaram C-80 calorimeter over the temperature range of 393 to 408 K. For a typical run, 20 mg samples of PETN were sealed in 0.15 cm³ stainless steel crucibles under an air atmosphere. For an induction time measurement, the sealed crucible was placed in the center of the C-80 detector, and data was collected until completion of the exotherm. Induction time was defined as the time-to-maximum rate (TMR).

The evolution of NO was recorded with a Shimadzu UV-260 spectrophotometer at 213 nm. Samples were prepared by loading 100 mg of PETN into 6 cm³ pyrex vessels attached to 1 cm cuvettes. The sample vessels were evacuated, sealed at 10⁻⁵ torr, and subjected to isothermal aging in a convection oven for 240 days. Periodically, the vessels were removed from the oven, and NO pressure was determined from the absorption band at 213 nm.

KINETIC MODELING

A semi-implicit Euler method [2] employing a step size of 10⁻⁷ was used to solve the problem of the initial value for decomposition of PETN under vacuum at 383 K. The model employed 29 species and 63 reactions. The proposed mechanism was based on the following initiation mechanism:

Reactions i to iii were proposed by W. L. Ng and coworkers [3]; reaction iv was postulated as an

alternative pathway for destruction of the tertiary radical, $\cdot\text{C}(\text{CH}_2\text{ONO}_2)_3$, formed in reaction ii. Reactions i to iii were assumed to arise from the solid state; the remaining secondary reactions, which lead to the observed product distribution for PETN decomposition (primarily CO , CO_2 , H_2O , N_2O , NO_2 , NO , N_2 , H_2CO), were assumed to arise from decomposition of CH_3ONO_2 and $\cdot\text{CH}_2\text{ONO}_2$ in the gas phase.

RESULTS

Representative thermograms for decomposition of PETN at 398 K with two different surface areas are illustrated in Figure 1. In order to quantify the temperature dependence of TMR, the apparent reaction rate was expressed as

$$\frac{d\alpha}{dt} = A 10^{-\frac{E}{\theta}} f(\alpha) \quad (1)$$

where $d\alpha/dt$ is the dimensionless rate

A is the apparent pre-exponential factor

E is the activation energy

$f(\alpha)$ is a function related to the reaction mechanism

θ is 2.303RT kJ/mole.

Rearrangement of Equation 1 and integration from 0 to the time-to-maximum rate yields

$$\log[\text{TMR}^{-1}] = \log A [\int f(\alpha_m)^{-1} d\alpha]^{-1} - \frac{E}{\theta} \quad (2)$$

where α_m is the extent of reaction at the TMR. Equation 2 indicates that a plot of $\log [\text{TMR}^{-1}]$ versus the reciprocal of absolute temperature should yield a straight line with a slope of $-E/(3.303R)$ and an intercept of $\log A [\int f(\alpha_m)^{-1} d\alpha]^{-1}$. A rate plot based on Equation 2 is illustrated in Figure 2.

Figure 3 shows reaction profiles for the evolution of NO from PETN with an initial surface area in the range of 3600 to 5000 cm^2g^{-1} determined at 383 K under vacuum by

UV at 213 nm. Figure 4 is a comparison of the NO evolution for PETN with initial surface area of $3600 \text{ cm}^2\text{g}^{-1}$ to results of kinetic modeling for PETN under vacuum and/or 20 torr of NO_2 .

DISCUSSION

Figures 1 and 2 reveal that TMR is correlated to surface area: TMR increases with the surface area. The breadth of the temperature range for the data given in Figure 2 prohibits a totally quantitative analysis; however, two points are significant. First, the apparent slopes for the data suggest that each sample reacts with different A and E parameters; variations of activation parameters with surface area are contrary to expectations that decomposition occurs homogeneously with E equivalent to the O- NO_2 bond fission enthalpy [1,3]. The $5000 \text{ cm}^2\text{g}^{-1}$ PETN is the only sample indicative of activation parameters consistent with homogeneous bond fission.

Secondly, at the high end of the temperature range, the data suggests coalescence to a common point; this indicates that reactivity is independent of initial surface area and residual solvent content at high temperature. It is well established that thermal aging of PETN is accompanied by a rapid decrease in surface area. These observations suggest that PETN reactivity is governed by (1) thermally-induced changes in surface area with concurrent production of crystal imperfections at the surface perturbed by differences in stabilizers and (2) residual solvents. Thermal aging would minimize the surface's free energy, decrease the surface area, and increase the mean particle size of PETN. Free energy minimization would be dominated by an increase in lattice entropy and increase the number of sites within the lattice available for decomposition. This mechanism is in accord with Myers [4] correlation between reactivity and particle size, and the crystal habit study of Rogers and Dinegar [5].

Profiles for NO evolution at 383 K given in Figure 3 for PETN with initial surface areas of 3600 and $5000 \text{ cm}^2\text{g}^{-1}$ suggest a stability order that may differ from that indicated by TMR data discussed above. Myers [4] measured gas evolution at 393 K for individual PETN crystals of specified particle size and concluded that reaction rates were directly proportional to particle size. However, NO_2 evolution determined at 323 K by

Volltrauer [6] and more recent NO evolution data determined at 363 K by Dosser indicates enhanced reactivity with higher surface area. Below 383 K, thermal microscopy indicates that aging of PETN with high surface area may produce additional crystal imperfections as the mean particle size increases and the surface area degrades. This phenomenon would lead to additional surface-active sites; therefore, the apparent correlation between stability and surface area suggested by TMR data could be altered at a lower temperature.

Figure 4 reveals that agreement between observed and calculated NO evolution is reasonable. The calculated profile for NO evolution for PETN under an initial pressure of 20 torr of NO_2 indicates that NO_2 accelerates the production of NO. This prediction has been recently confirmed by Dosser; consistency between prediction and experiment adds credibility to the detailed mechanism used in the kinetic modeling. The kinetic model also provides a quantitative explanation for the fact that TMR is reduced when NO_2 (adsorbed on the PETN surface) and/or O_2 are present in the atmosphere. Here, secondary reactions, arising from chain initiation by NO_2 or oxidation of NO by O_2 , reduce the magnitude of the differential, $f(\alpha)^{-1}d\alpha$, which leads to a smaller TMR.

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Fig. 2 Effect of Surface Area upon NO Evolution from PETN at 383K

Fig. 3 TMR Plot for PETN Decomposition from 383 to 408 K

Fig. 4 Comparison of Calculated and Observed NO/NO₂ Evolution Profiles from PETN at 383 K

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