

The thermal decomposition of energetic materials. Part 64. Kinetics of decomposition of furazano[3,4,*b*]piperazine and its 1,4-dinitro nitramine derivative

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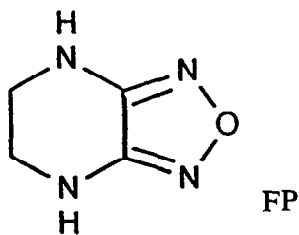
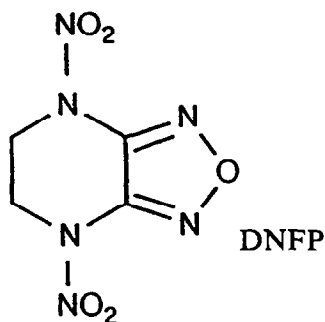
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Abstract

The Arrhenius kinetics of decomposition of the nitramine explosive 1,4-dinitrofurazano[3,4,*b*]piperazine (DNFP) and the less energetic parent amine furazano[3,4,*b*]piperazine (FP) were determined by isothermal TGA and from the rate of change of selected vibrational modes in the IR spectra. For DNFP, $E_a = 136$ kJ and $\log A = 15.5 \text{ min}^{-1}$. The IR spectra show that N–NO₂ homolysis is the dominant initial reaction. For FP, $E_a = 202$ kJ and $\log A = 22.1 \text{ min}^{-1}$. The value of E_a is the same as the N–O bond strength of the furazan ring.

INTRODUCTION

Compounds containing the furazan ring decompose exothermically and have, therefore, potential interest in the explosives and solid rocket-propellant fields. The relatively high density and stored energy of 1,4-dinitrofurazano[3,4,*b*]piperazine (DNFP) make it an attractive energetic molecule [1–4]. A detailed study has been made of the crystal structure, solid–solid



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phase transitions and rapid thermal decomposition of DNFP [5]. However, the kinetics of its decomposition are unknown. The gas products suggest that N–NO₂ homolysis dominates in the early decomposition process. However, furazano[3,4,*b*]piperazine (FP) decomposes in a more complicated fashion as evidenced by the gas products [5, 6].

Some researchers believe that the rate of slow, lower temperature thermal decomposition of energetic molecules correlates with the explosive [7–10] and combustion characteristics [11]. However, care must be taken because this connection frequently does not exist [12]. In this paper, we wish to show that the thermal decomposition kinetics of DNFP and FP are different and relate to the structure and composition of the molecules.

EXPERIMENTAL

Samples of DNFP and FP were supplied by Dr. R.L. Willer of the Thiokol Corporation, Elkton, MD. Isothermal thermogravimetric analysis (TGA) was conducted in air on a DuPont Instruments 951 analyzer in the temperature range 388–403 K for DNFP and 428–443 K for FP. The sample size was 2–3 mg and the temperature control was $\pm 1^\circ\text{C}$.

The kinetics of decomposition of DNFP from the solid phase was studied in air in the 379–395 K range by transmission IR spectroscopy. DNFP was dissolved in acetonitrile and spread onto a NaCl plate. The solvent was then evaporated to leave the DNFP residue as a thin film. This plate was then placed uncovered in the solid-phase IR cell, described previously [13, 14], so that gases could escape. The temperature was then maintained isothermally by a time-proportioning controller. Thirty-two spectra were summed per file using a Nicolet 60SX FTIR spectrometer operating at 2 cm⁻¹ resolution. The rate of decrease in intensity with time of the –NO₂ asymmetric and symmetric stretching modes of the nitramine, and the CH₂ asymmetric stretch and bending modes, afforded the rate data.

KINETICS OF DECOMPOSITION

The decompositions of DNFP and FP were determined isothermally by TGA over a range of temperatures where the reaction is relatively slow. The rate of the initial 20–50% weight loss by gas evolution was calculated at each temperature from Figs. 1 and 2, and was fitted by eqn. (1)

$$\log(1 - \alpha) = kt + c \quad (1)$$

where $\alpha = (W_0 - W_t)/W_0$, t is time and k is the rate constant at a given temperature. W_0 is the initial sample weight and W_t is the weight at time t . Values of k are tabulated in Table 1. Plots of $\log(1 - \alpha)$ versus t (Figs. 3 and 4) are linear, indicating that a global first-order process is representative. The global activation energy E_a and pre-exponential factor A from an

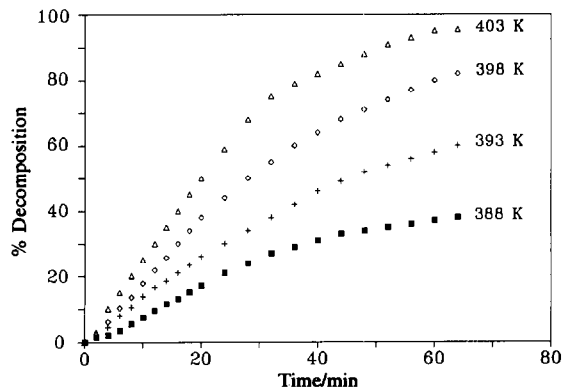


Fig. 1. The time dependence of the weight loss from DNFP determined by TGA.

Arrhenius plot of the rate constant at each temperature are given in Table 1. The accuracy of E_a is estimated to be $\pm 2 \text{ kJ mol}^{-1}$.

While the activation energy of a condensed-phase thermal decomposition process of a complex molecule is rarely the result of simple bond rupture, further insight into the molecular processes contained in the initial decomposition steps is obtained from transmission IR spectroscopy during the reaction. Because the spectral changes involve a decrease in intensity of modes due to gas-producing reactions, the solid phase IR transmission cell [13, 14] was designed to allow the gases to escape. Detailed IR spectra of DNFP have been analyzed before [5]. The modes assigned to the $-\text{NO}_2$ functional groups of DNFP are not pure because of coupling with the N–N bond [15]. The rate of decrease of the area B of these modes, however, qualitatively reflects cleavage of the N–N bond and liberation of $\text{NO}_2(\text{g})$. The rate constant k was calculated for the initial 50% of decomposition

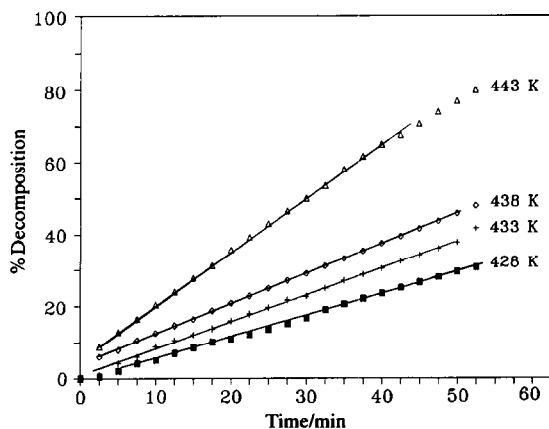


Fig. 2. The time dependence of the weight loss from FP determined by TGA.

TABLE 1

Rate constants and Arrhenius parameters for DNFP and FP

| T/K | $k \times 10^3/\text{min}$ | $E_a/(\text{kJ mol}^{-1})$ | $\log(A/\text{min}^{-1})$ |
|------|----------------------------|----------------------------|---------------------------|
| DNFP | | | |
| 388 | 4.0 | 136 | 15.5 |
| 393 | 6.6 | | |
| 398 | 11.0 | | |
| 403 | 18.0 | | |
| FP | | | |
| 428 | 2.0 | 202 | 22.1 |
| 433 | 3.8 | | |
| 438 | 4.7 | | |
| 443 | 10.5 | | |

from eqn. (1), where $\alpha = (B_0 - B_t)/B_0$. As with the TGA data, a first-order rate expression fits the change of absorbance. Table 2 gives the resulting Arrhenius constants. The kinetics of change of both the symmetric and asymmetric stretching modes of $-\text{NO}_2$ are the same within experimental error and closely resemble the Arrhenius values determined from the weight loss. This is good evidence that the rate of $\text{N}-\text{NO}_2$ homolysis dominates the rate of thermal decomposition of DNFP in this temperature range. Conversely, the kinetic constants for the decrease in the area of the CH_2 asymmetric stretch are very different from the kinetics of overall weight loss, indicating that $\text{C}-\text{H}$ homolysis does not dominate the rate of decomposition in this temperature range. The decomposition of the $\text{C}-\text{H}$ bond is not likely to involve simple homolysis in these compounds, but might rather be a bimolecular, concerted process in the condensed phase.

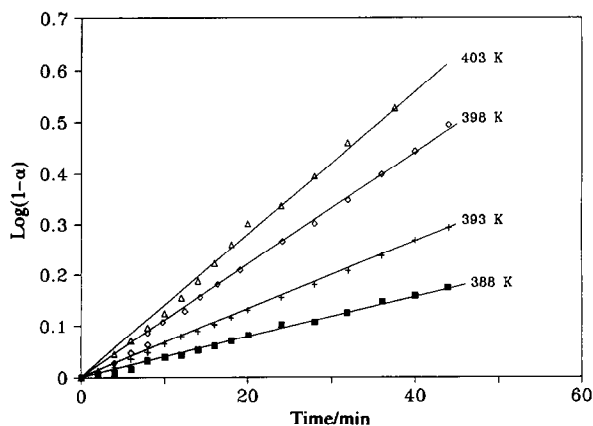


Fig. 3. Rate constant plots for the initial 50% of decomposition of DNFP.

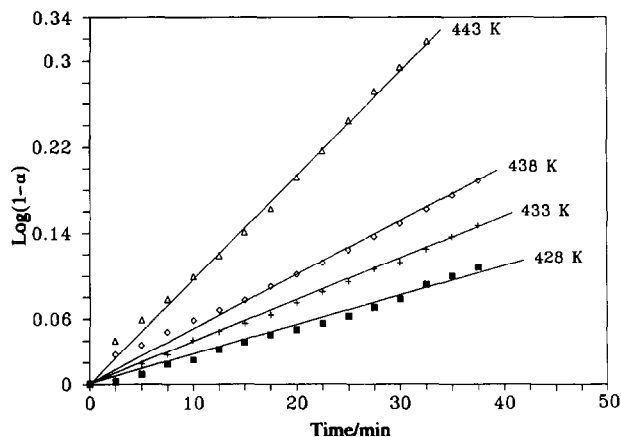


Fig. 4. Rate constant plots for the initial 50% of decomposition of FP.

The global activation energy for decomposition of DNFP is somewhat lower than the N–NO₂ bond dissociation energy of a secondary nitramine (190–210 kJ) [16]. However, the molecular structure of DNFP reveals that the C₂NNO₂ linkage is not a typical secondary nitramine [5]. The C–N bond distance to the carbon atom of the furazan ring is rather short, indicating multiple bond character, while the C–N bond distance to the ethylene carbon atom is typical of a C–N single bond. Hence, there is *nitrimine* character in the nitramine unit. Nitrimines have a bond dissociation energy of approximately 155 kJ mol⁻¹ [16]. This ground-state distribution of electron density in DNFP is also reflected in an anomalously long N–N bond and a tendency to release a large amount of NO₂ upon fast thermolysis [5, 17, 18].

Furazanopiperazine is the parent amine of DNFP and lacks the –NO₂ groups. The kinetic constants for the initial 50% of decomposition of FP are given in Table 1. While the activation energy resembles the values obtained for the CH₂ unit of DNFP, we regard this similarity as coincidental. A more probable reason for the activation energy value of FP is the decomposition

TABLE 2

Arrhenius parameters for decrease in absorbance of characteristic vibrational modes as determined isothermally by IR spectroscopy

| Wavenumber | Mode | E_a /kJ mol ⁻¹ | log(A /min ⁻¹) |
|------------|-------------------------|-----------------------------|-------------------------------|
| 1597 | $\nu_{as}(\text{NO}_2)$ | 140 | 15.5 |
| 1315 | $\nu_s(\text{NO}_2)$ | 136 | 15.7 |
| 1267 | $\nu_s(\text{NO}_2)$ | 138 | 15.6 |
| 3028 | $\nu_{as}(\text{CH}_2)$ | 200 | 22.5 |
| 867 | $\delta(\text{CH}_2)$ | 199 | 22.5 |

of the furazan ring at the weakest bonds. In particular, the N–O single-bond energy is 200 kJ [19]. This value closely resembles the activation energy of thermal decomposition of FP. Vibrational spectroscopy is not especially helpful in substantiating the dominance of cleavage of an N–O bond in the initial decomposition stage of FP because no pure vibrational motion dominates the furazan ring [20]. Extensive coupling exists, so that almost all of the modes will change simultaneously and in a complex manner upon thermal decomposition.

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