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KINETIC STUDIES OF THE THERMAL DECOMPOSITION OF KDNBF, A PRIMER FOR EXPLOSIVES

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Abstract

KDNBF (potassium 4,6-dinitrobenzofuroxan) has been used as a primer explosive in igniters and detonators for many years. Considerable information about the sensitivity of KDNBF to various stimuli, such as impact, friction, shock and electrostatic charge, is known. However, the thermal sensitivity of KDNBF has been relatively unexplored. Hence, there is very little information available concerning the fundamental thermal properties of KDNBF. Therefore, as part of an extensive thermal hazard assessment, DSC, TG, accelerating rate calorimetry (ARC) and heat flux calorimetry (HFC) measurements have been undertaken on KDNBF. The results demonstrate that KDNBF decomposes via a multi-step exothermic process directly from the solid state. The decomposition process does not appear to depend on the nature of the atmosphere, except in the final stage of the TG decomposition in air, where remaining carbonaceous material is converted to CO_2. The first stage of the decomposition is sufficiently rapid that ignition occurs if too large a sample is used. Dynamic and isothermal methods were used to obtain the kinetic parameters and a range of activation energies were obtained, depending on the experimental conditions. The kinetic results have been analyzed in terms of various solid state decomposition models.

Keywords: ARC, DSC, HFC, KDNBF, TG

Introduction

The potassium salt of 4,6-dinitrobenzofuroxan (KDNBF) (Fig. 1) is more stable and less impact sensitive than the parent compound [1]. Consequently, it is often used in primary explosive and propellant compositions. In spite of its continuous use in these applications for many years, very little is known about the thermal properties of KDNBF.

A report by Rouch and Maycock [2] describes DTA and TG results for KDNBF. They observed a decrease in the DTA peak temperature of about 25°C after KDNBF had been subjected to two cycles of 64 h ‘sterilization’ in air at 125°C. The authors claim that KDNBF detonates at 200°C and reported conflicting results from isothermal TG studies, except under continuously pumped vacuum conditions, from which experiments the kinetic parameters, E_a=126 kJ mol^{-1} and lg(A/min^{-1})=32.0 were obtained, where E_a is the activation energy and A is the pre-exponential factor in the

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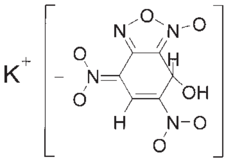

Fig. 1 Structure of potassium 4,6-dinitrobenzofuroxan

Arrhenius equation. Accelerated aging at 86°C showed a continuous gradual mass loss reaching about 17% after 240 days but the DTA thermal curve showed no significant change from the untreated material.

An 'ignition temperature' of 200°C [3] has been determined for KDNBF in an experiment in which an unconfined 50 mg sample was heated at 5°C min^{-1}. This publication also reports E_a=179 kJ mol^{-1} and lg(A/min^{-1})=43.2, determined from non-isothermal DSC studies on 0.2 mg samples in aluminum pans having unsealed lids.

Because of the limited and conflicting information available in the literature, a fundamental study of the thermal properties of KDNBF was initiated. Hence, this paper will report results of DSC, TG, ARC (accelerating rate calorimetry) and heat flux calorimetry (HFC) measurements on KDNBF and a discussion of these results in terms of solid phase decomposition models.

Experimental

Materials

KDNBF was supplied by Stresau Laboratory Inc. and was shown by NMR measurements to be at least 99 mol% pure. No additional purification was conducted on KDNBF prior to its use in the experiments described below.

DSC and TG

A TA 2100 Thermal Analysis System with modules for DSC (2910) and TG (2950) was used for these measurements. Dry, oxygen-free, nitrogen was used to purge the DSC at 50 cm^3 min^{-1} and the TG at 60 cm^3 min^{-1} in the furnace and 40 cm^3 min^{-1} in the balance, for a total of 100 cm^3 min^{-1}. Heating rates, β from 0.2 to 10°C min^{-1} were employed and sample sizes were about 0.2 and 1 mg, respectively, for the DSC and TG measurements.

Sealed glass microampoules were used in the DSC experiments conducted at ambient pressure and aluminum pans with lids having laser-produced pin holes were used for measurements at pressures up to about 6.8 MPa with a TA pressure cell. TG experiments under isothermal and non-isothermal conditions were carried out with a platinum sample boat.

The microbalance of the TG module was calibrated *vs.* a Mettler M3 electronic microbalance with a reproducibility of ±1 μg and both the DSC and TG modules were calibrated using ASTM procedures [4–5] before the experiments.

ARC

In the experiments using ARC, 0.1 or 0.5 g of KDNBF was placed in lightweight, spherical titanium vessels, which formed part of a closed system thereby maintaining any pressure resulting from vaporization and decomposition of the sample. A leak test was carried out before each experiment. The experiments were conducted in duplicate, both in an inert atmosphere and in air. The standard ARC procedure was used: the temperature of the system was raised by 5°C and the system was kept adiabatic firstly until thermal transients disappeared and, finally, while a 'search' was made for an exotherm, defined as a self-heating rate, $R \geq 0.02°C\ min^{-1}$. The temperature at which this occurs is a measure of the onset temperature for the exotherm. As well, a number of isothermal experiments were conducted at temperatures below the onset temperature.

HFC

The manifold and special high pressure vessels for HFC measurements are described in [6]. Samples of about 10 mg of KDNBF were sealed in glass ampoules having internal volumes of about 0.7 cm^3. The glass ampoule was loaded in the high pressure vessel and a helium environment was used to provide good thermal conductivity between the ampoule and the vessel. Heating rates, β ranging from 0.09 to 2°C min^{-1} were used in the HFC experiments, from which kinetic parameters were estimated using ASTM E 698 [7].

Results and discussion

DSC and TG

The DSC and TG (in N_2 and in air) curves for KDNBF at 5°C min^{-1} are compared in Fig. 2. The DSC results indicate that a solid phase decomposition occurs in a complex pattern with a major exotherm accompanied by one or more minor exotherms. The reaction causing the major exotherm appears to be very rapid. An onset temperature of 195±5°C was determined from the point where the first significant deviation from the baseline occurred. It was not possible to achieve consistent results from variable heating rate studies in the DSC using established experimental procedures [8].

Figure 3 compares the DSC curves of KDNBF obtained at pressures up to 6.89 MPa with that obtained using the glass microampoule. No significant variation in the peak temperature of the main exotherm was observed.

The TG results in Fig. 2 show that decomposition occurs in at least two stages and that the first stage is rapid compared with subsequent step(s). Assuming that the initial mass loss follows a first order rate law, leads to the conclusion that the latter processes are higher order reactions. At temperatures above about 300°C, some oxidation is evident from the experiments conducted in air.

Kinetic parameters were determined from a series of non-isothermal experiments and the results are illustrated by Fig. 4, which shows a plot of $\lg(\beta/K\ min^{-1})$ *vs.*

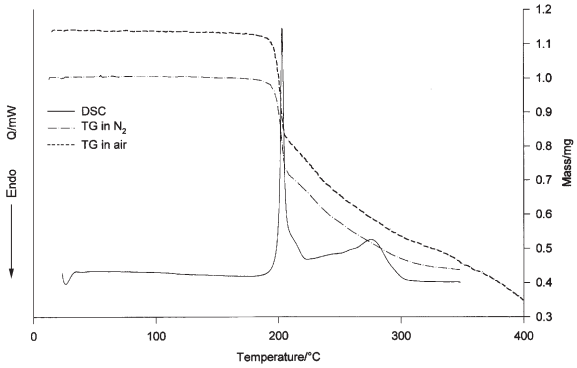

Fig. 2 DSC and TG results for KDNBF at β=5°C min^{-1}

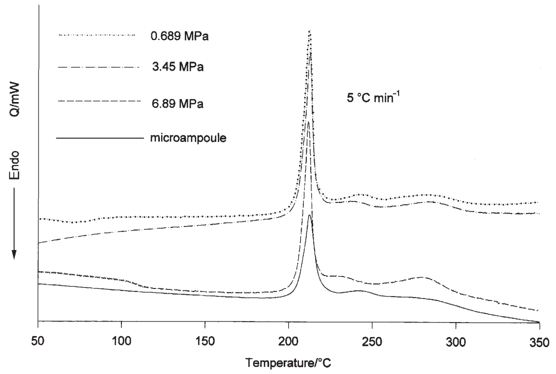

Fig. 3 Comparison of DSC results in microampoule and in hermetic pan at pressures up to 6.89 MPa

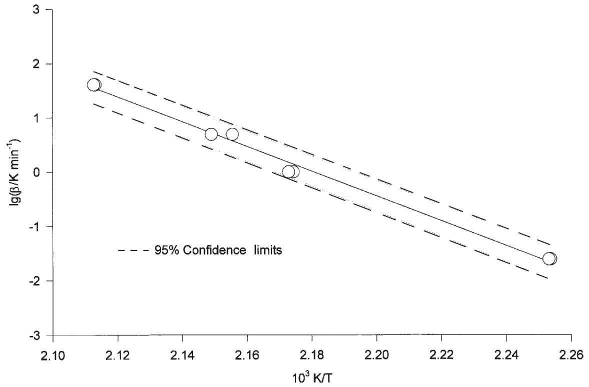

Fig. 4 TG kinetic results at 10 mass% using ASTM E1641

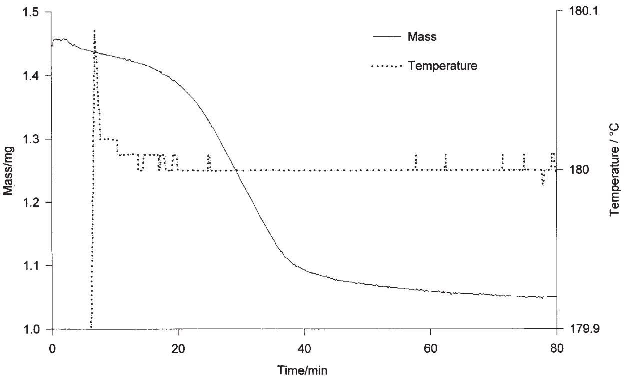

Fig. 5 TG results at T=180°C

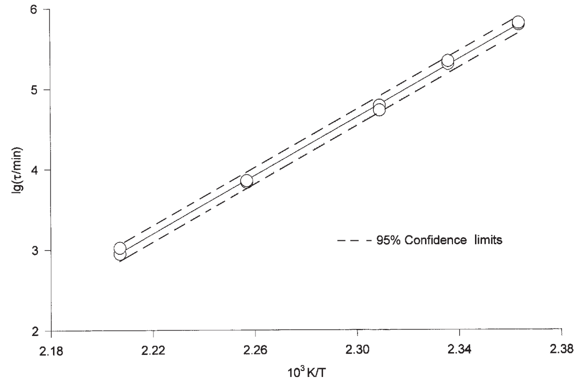

Fig. 6 Kinetic results obtained from isothermal TG data using induction time

reciprocal temperature at 10 mass % conversion of KDNBF. The kinetic parameters determined from this analysis [9] are E_a=190±6 kJ mol^{-1} and lg(A/min^{-1})=46.6±0.3.

Additionally, isothermal TG measurements were conducted on KDNBF between about 150 and 180°C. In each experiment, a temperature dependant induction period was followed by a linear mass loss i.e. zero order. For all temperatures studied, 22±3% mass loss occurred in the linear region prior to a plateau in the mass–time dependancy. This behaviour is illustrated in Fig. 5 for T=180°C. The induction time, τ was determined from the intersection of the extrapolated initial baseline and the linear portion of the mass loss. Subsequently, 1g(τ/min) was plotted *vs.* the reciprocal isothermal temperature, as in Fig. 6, to obtain E_a=151±2 kJ mol^{-1}. Analysis of the zero order results yielded E_a=173±2 kJ mol^{-1} and lg(A/min^{-1})=41.9±0.6.

ARC

Figure 7 illustrates the temperature and pressure results obtained from a ‘heat-wait-search’ experiment conducted on a 0.1 g sample of KDNBF. An onset temperature of

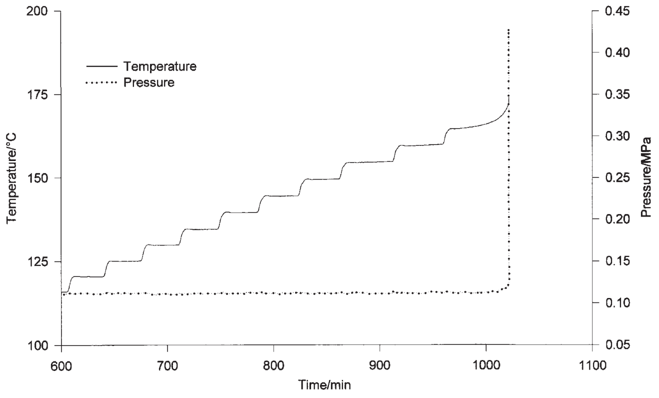

Fig. 7 ARC results using 0.1 g KDNBF

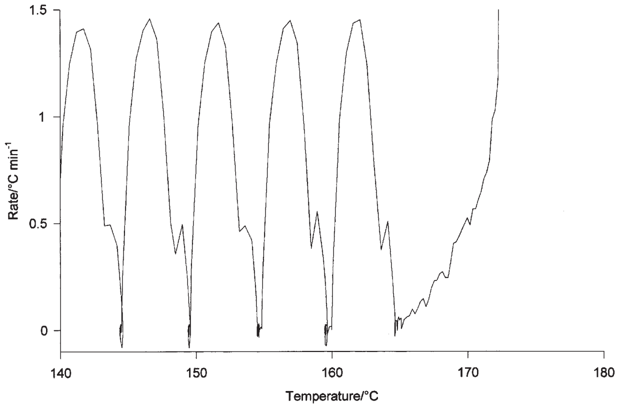

Fig. 8 Self-heating rate for 0.1 g KDNBF

T_0=162±5°C was determined by extrapolating the ARC-detected values to R=0, as shown in Fig. 8, for a series of tests. No variation in T_0 was observed for experiments performed in air or argon or using initial temperatures of 35 or 100°C.

In an experiment with 0.5 g of KDNBF, T_0 was found to be 148±5°C, hence it appears that this parameter is mass dependant. In this case, the rate of the decomposition of KDNBF accelerated to runaway shortly after the exotherm was detected by the ARC (Fig. 9) and the titanium vessel ruptured.

ARC results for KDNBF using isothermal studies at a nominal temperature of 150°C are illustrated by Fig. 10. Similar results were obtained for temperatures from 140 to 155°C. While there is characteristically some drift in the isothermal temperature used in the ARC, it was still possible to estimate the time for reaction to occur, and determine E_a=189±6 kJ mol^{-1}, from a plot of 1g(τ/min) *vs.* the mean isothermal temperature, as shown in Fig. 11.

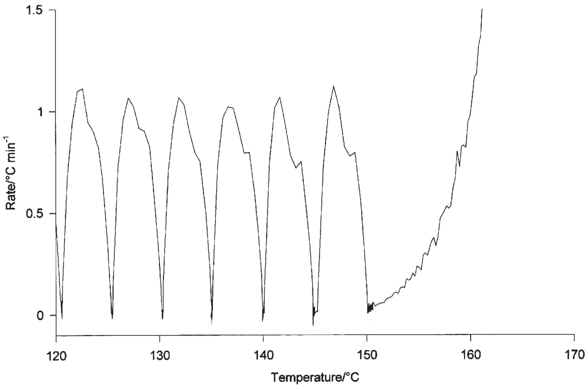

Fig. 9 Self-heating rate for 0.5 g KDNBF

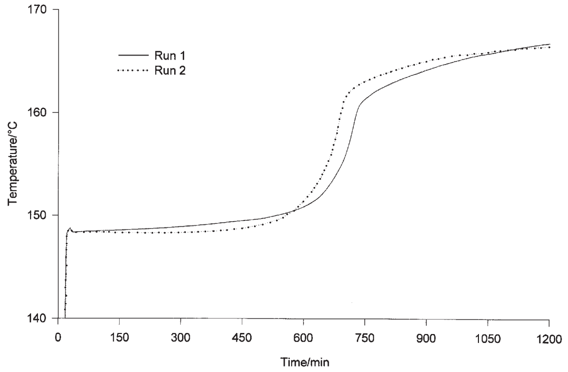

Fig. 10 ARC results at a nominal temperature of 150°C

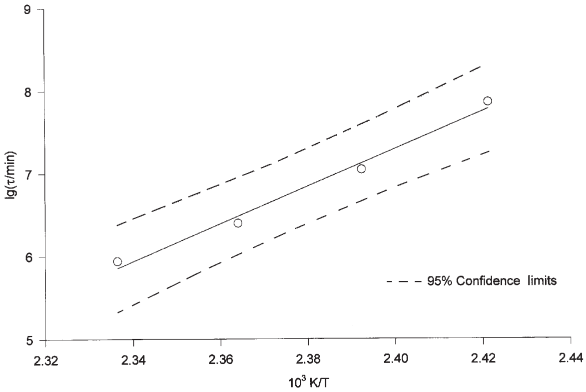

Fig. 11 Kinetic results obtained from isothermal ARC data using induction time

HFC

Figure 12 depicts HFC results obtained for KDNBF using a 10 mg sample and a heating rate, β=0.3°C min^{-1}. The onset temperature obtained from HFC is 170±5°C, similar to that obtained using 0.1 g KDNBF in the ARC measurements. There is sufficient separation between the main and subsequent exotherms to allow a precise value of ΔH=2.10±0.05 kJ g^{-1} to be determined for the former exotherm, in contrast with the results obtained from the DSC experiments.

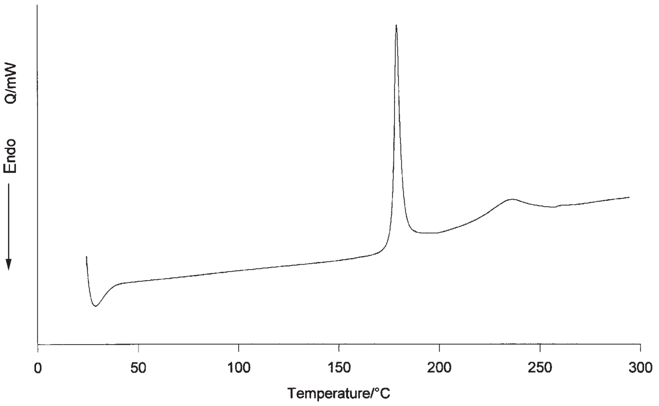

Fig. 12 HFC reuslts for 10 mg KDNBF at β=0.3°C min^{-1}

From the heating rate experiments, a plot of $\lg(\beta/T_m^2)$ *vs.* T_m^{-1}, where T_m is the peak temperature (corrected for thermal lag), as shown in Fig. 13, was used to determine E_a=132±4 kJ mol^{-1} and assuming a first order process, $\lg(A/\mathrm{min}^{-1})$=21.7±0.2.

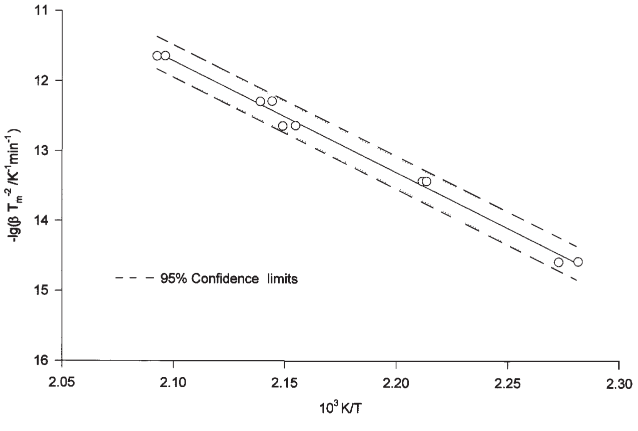

Fig. 13 Kinetic results obtained from HFC data using ASTM E698

Comparison of results

The kinetic parameter data taken from the literature and those determined in this work are compared in the Table 1. It appears that the differences in the data listed in the Table 1 are, at least partially, a result of significant variations in experimental conditions, such as the nature of the system, sample size, heating rate, etc. There is reasonable agreement between the literature DSC, the dynamic TG, the zero order isothermal TG and the ARC isothermal results, considering the uncertainties in these results. In contrast, the data derived from the literature isothermal TG and HFC results stand out as uniquely different, the former apparently because of the substantially reduced possibility of any influence of volatile products and the latter likely because of the large mass/volume ratio.

Table 1 Comparison of kinetic parameters obtained for KDNBF using a variety of thermal techniques

Method		E_a/kJ mol^{-1}	lg(A/min^{-1})
Literature			
TG isothermal [2] 3 mg vacuum continuously pumped		126	32.0
DSC dynamic [3] 0.2 mg unsealed lids		179	43.2
This work			
TG dynamic; 1 mg ASTM E 1641		190	46.6
TG isothermal 1 mg	τ	151	–
	zero order	173	41.9
ARC isothermal 100 mg τ		189	–
HFC dynamic 10 mg ASTM E 698		132	21.7

Conclusions

KDNBF undergoes thermal decomposition directly from the solid phase, thereby allowing test of various solid phase kinetic models. The decomposition path of KDNBF does not appear to be determined by the nature of the gas environment. In a closed system, with minimum free volume, the decomposition of KDNBF is apparently autocatalytic. Autocatalytic decomposition of KDNBF results in a significantly lower activation energy than for open systems or those closed systems with large free volume.

Specifically, the activation energy determined from the HFC measurements is significantly lower than that obtained from the TG and ARC results. This can at least partially be accounted for by the different experimental conditions used in each of these techniques. TG is conducted in an open system with gas flow so that gaseous decomposition products are removed as formed while both the ARC and HFC are closed systems. The mass to free volume ratio used in the HFC studies is more than double that in the ARC measurements, hence a higher pressure and an enhanced autocatalytic effect from the gaseous decomposition products is achieved in the HFC system.

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