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STUDY ON THE DECOMPOSITION KINETICS OF FOX-7 AND HNF

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Abstract

At TNO Prins Maurits Laboratory the characterisation and application of energetic materials is one of the main research topics. In this respect, the activities are focussed on using thermal analysis techniques such as TG/DTA and DSC. Standard DSC and TG/DTA techniques usually apply a linear temperature increase. During this gradual temperature change, the sample may pass certain phase changes related to different crystal structures, followed by a melting/decomposition of the material. In this way physicochemical properties like phase change temperatures, melting point, enthalpy of melting, decomposition temperature, etc. can be determined. By applying different heating rates, an analysis of the decomposition kinetics can be performed as well, which gives additional information on the decomposition process of the material. In this way the activation energy of the decomposition process and the 'shelf-life' of the material, when stored at a certain temperature, can be assessed.

In a co-operation with the Technical University of Aachen, two relatively new and promising energetic materials were investigated: FOX-7 and HNF. FOX-7, or 1,1-diamino-2,2-dinitroethylene, is a less sensitive explosive, which could find application as a substitute of RDX (less sensitive but with preservation of performance).

Hydrazinium nitroformate (HNF) is an oxidiser with potential use as a high-performance, chlorine-free ingredient in rocket propellants.

The results of the TG/DTA and DSC tests, as well as the results of the analysis of the decomposition kinetics of these two materials, will be reported and discussed in this paper.

Keywords: decomposition, energetic materials, kinetics, lifetime, TG/DTA

Introduction

During this study two energetic materials were investigated by thermal analysis (TG/DTA) to perform kinetic analyses.

FOX-7 (1,1-diamino, 2,2-dinitro ethene) is considerably less sensitive than RDX (hexogene) but with similar performance aspects. It consists of yellow-orange crystals, with a density of 1.885 g cm^{-3}. The material used in this investigation is synthesised at FOI (Sweden).

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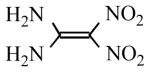
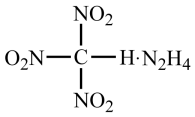
The raw material, recrystallised and re-precipitated products do not seem to contain any impurities, though differences have been observed in their thermal behaviour.



Molecular formula	$C_2N_4H_4O_4$
Molecular mass	148 g mol^{-1}
Appearance	yellow-orange crystal
Crystalline form	monoclinic (α-phase)
Melting point	270°C (decomposition)
Density	1.885 g cm^{-3}

HNF (Hydrazinium Nitroformate) is a yellow, crystalline material, which is manufactured by Aerospace Propulsion Products (APP) in The Netherlands. HNF is an energetic material to be used as an oxidiser in solid propellant or as a monopropellant. Since HNF does not contain any chlorine, also its combustion products do not contain any chlorine gases.



Molecular formula	$N_2H_5C(NO_2)_3$
Molecular mass	183.08 g mol^{-1}
Appearance	yellow crystal
Crystalline form	monoclinic
Melting point	~124°C
Combustion energy	–5824 kJ kg^{-1}
Density	1.86 g cm^{-3}

Modern solid rocket motors are generally based on ammonium perchlorate (AP) in a hydroxy-terminated polybutadiene (HTPB) binder system. Replacement of the AP with HNF will, as indicated above, result in performance gains, chlorine free exhaust products, and a reduced smoke signature; whereas it represents a relatively small change in composite propellant production (all existing knowledge and production infrastructure for HTPB based systems can be kept in place [2, 3]).

Thermoanalytical studies

DSC and TG/DTA are techniques that are generally used and well known. The experimental equipment comprises a TG/DTA-320 and a DSC-220-C, both manufactured by Seiko Inc. Open aluminium cups were used and a heating rate of 2 to 10°C min^{-1} was applied for the kinetic measurements with the TG/DTA. The temperature range was from room temperature to ~300°C.

The kinetic studies were performed only with the TG/DTA equipment.

FOX-7

FOX-7 is transported in water. In order to check any influence of the presence of water on the properties of FOX-7, both wet and dry samples were tested (Table 1).

Table 1 Overview of the onset temperature resulting from the TG/DTA measurements

Sample	Mass/mg	Carrier gas	β/°C min^{-1}	T_0 endo/°C			T_0 exo/°C		Mass change/%m/m	
				1	2	3	1	2	1	2
wet	4.600	N_2	10	99.0	–	–	275.4	–	32.92	42.97
wet	3.908	N_2	10	98.8	–	–	275.8	–	37.77	46.30
wet	4.344	air	10	99.2	–	–	275.7	–	36.82	47.85
wet	4.354	air	10	99.1	–	–	275.7	–	36.55	48.47
wet	4.754	N_2	2	98.8	–	–	–	–	82.31	–
wet	5.076	N_2	2	98.8	–	–	–	–	81.51	–
dry	2.488	N_2	10	99.3	113.3	169.4	216.1	278.6	14.09	57.90
dry	2.239	N_2	10	98.8	112.7	168.1	214.9	281.5	12.88	58.45
dry	2.590	N_2	5	99.4	112.8	168.2	208.9	–	11.74	59.61
dry	2.336	N_2	5	98.7	112.3	170.2	208.6	–	11.63	60.27
dry	2.788	N_2	2	99.1	112.4	–	–	–	11.54	61.22
dry	2.693	N_2	2	99.0	112.0	–	–	–	11.75	61.10

The resulting curves are presented below. In Fig. 1 a comparison is made between a 'wet' and 'dry' sample.

This work is performed with two heating rates, 10°C min^{-1} and 2°C min^{-1}, respectively.

Based on the curves in Fig. 1 it could be concluded that there is a difference between 'wet' and 'dry'. The DTA curve of the 'wet' curve shows a small endotherm around 100°C, which is not observed with the 'dry' sample.

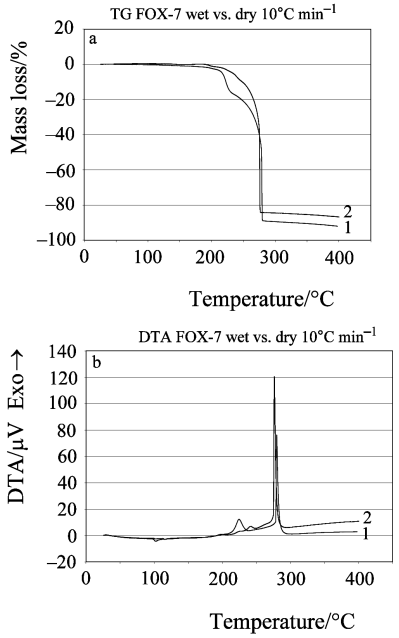


Fig. 1 Comparison of 'wet' and 'dry' raw material. a – TG signal, b – DTA signal; curve 1 – dry, curve 2 – wet

After the TG/DTA measurements on the 'wet' FOX-7, additional DSC experiments were performed to investigate the endotherm effect which occurs at ~100°C in order to investigate this effect in more detail. If this would be a phase-transition, this would become clear in cyclic DSC measurements in a temperature range of 60 to 120°C. By repeating these cycles a few times, it is possible to see whether or not this transition is reversible. In case of a phase transition the endothermal effect will return each time, at the same temperature. In case the endothermal effect is caused by an impurity, the endotherm can be correlated to evaporation and then the effect will occur only once. The additional DSC tests indicated that the effect only takes place once, and after a few cycles it disappears. So it is not a phase transition, but probably caused by an effect of the used solvents.

DSC-curves of raw product(s) do not reveal good reproducibility and usually have a weak endotherm with the peak moving from 95 to110°C, depending on the history of the product;

• three exotherms are seen in most cases: two weak ones at 200 and 245°C, respectively, and a very strong one with the peak position at ca. 270°C.

On the contrary, recrystallised or reprecipitated products, independent of the type of the solvent used, are characterised by two nicely reproducible endotherms:

• one pronounced at 118°C and another one, rather weak, at ca. 165°C.
• Two exotherms are usually present in the curves: one broad with the peak at 245°C and another sharp with the peak at 275–280°C.

All these phenomena indicate the occurrence of phase transitions which are due to differences in the crystal structure of the product [5].

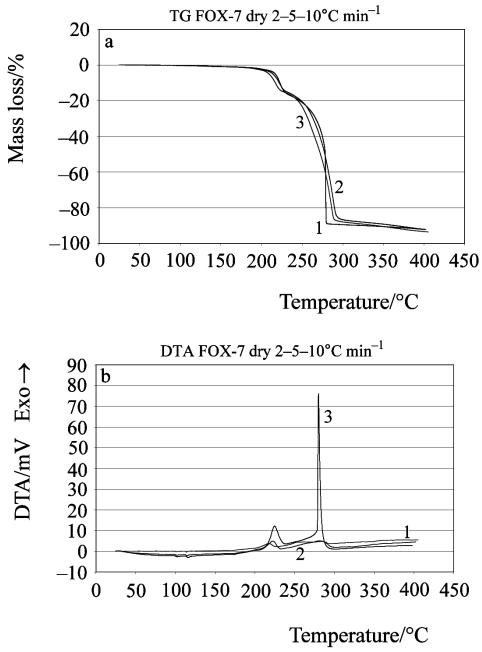


Fig. 2 TG and DTA curves on raw FOX-7 'dry' with different heating rates. a – TG signal, b – DTA signal; curve 1 – 2°C min^{-1}, curve 2 – 5°C min^{-1} and curve 3 – 10°C min^{-1}

The curves shown in Fig. 2 show the TG/DTA curves for FOX-7, recorded at three different heating rates (2, 5 and 10°C min^{-1}). These curves will be used for the kinetic studies and will be discussed in the next section.

HNF

The DSC measurements were performed with a heating rate of 5°C min^{-1}. In the case of the DSC experiments closed SuS-vessels were used. They can withstand a pressure of about 80 bars.

Table 2 Results of TG/DTA and DSC experiments on HNF

TG/DTA	DTA-onset/°C	129
	Mass change/%	97
	Enthalpy/μV s mg^{-1}	~1040
DSC	Melting point/°C	123.8–124.4
	DSC-onset/°C	125.4–126.1
	Enthalpy/mJ mg^{-1}	3961–4035

According to the results in Table 2 and Figs 3 and 4, it can be concluded that immediately after an endothermal effect, an exothermal effect occurs. Two grades of HNF have been studied: an S and an E type [1], referring to their production techniques (solvent/non-solvent and evaporative crystallisation, respectively). The enthalpy as given by TG/DTA is only an indicative value, because all the measurements are performed in open cups.

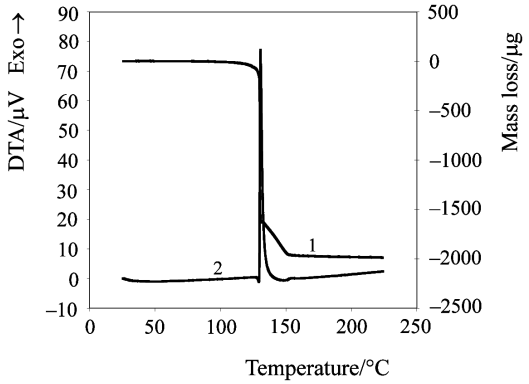


Fig. 3 TG/DTA cure of HNF. Curve 1 – TG and curve 2 – DTA

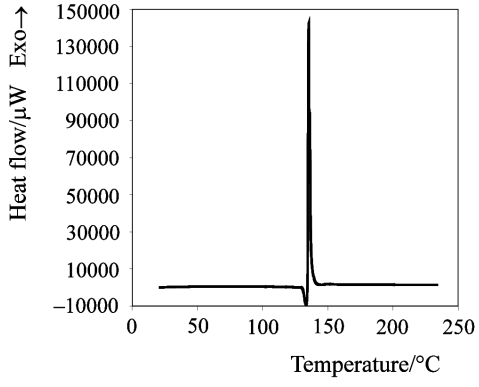


Fig. 4 DSC curve of HNF

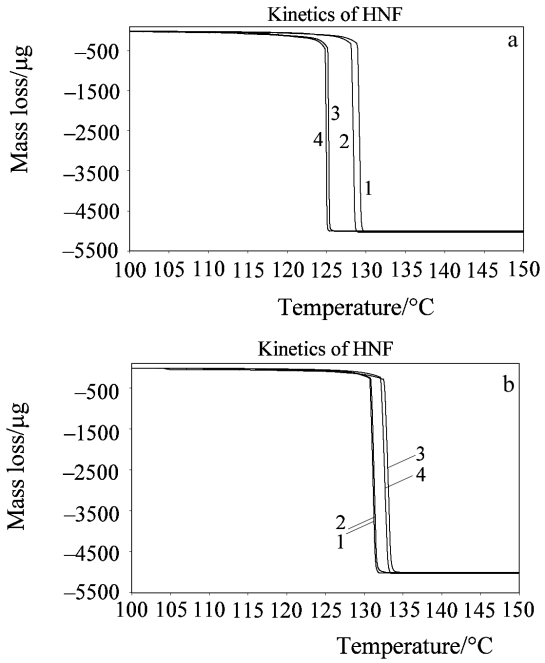


Fig. 5 TG curves on HNF with different heating rates for kinetics. a – curve 1 – TG signal 5°C min^{-1}, curve 2 – TG signal 5°C min^{-1}-2, curve 3 – TG signal 2.5°C min^{-1}-1, curve 4 – TG signal 2.5°C min^{-1}-2; b – curve 1 – TG signal 7.5°C min^{-1}-1, curve 2 – TG signal 7.5°C min^{-1}-2, curve 3 – TG signal 10°C min^{-1}-1 and curve 4 – TG signal 10°C min^{-1}-2

The curves shown in Fig. 5 will be used for the kinetic studies and will be discussed in the next section.

Kinetic studies

The kinetic studies (shown in Figs 2 and 5 for FOX-7 and HNF, respectively) are analysed by means of the following methods:

- Kissinger method,
- Modified Flynn–Wall–Ozawa method and
- Friedman method.

By means of these kinetic studies, information is obtained about the decomposition behaviour of the material under investigation. The decomposition process can be characterised by three parameters: the activation energy (parameter E), the order of reaction (parameter n) and pre-exponential factor (parameter A).

We have used both the integral (the modified Flynn–Wall–Ozawa method [4]) and the differential (Friedman method) iso-conversional methods for better discriminating among various possible mechanisms of the decomposition process. It is known

that when the values of parameter *E*, calculated by any iso-conversional method, show a clear dependence on the conversion degree, one may suppose the occurrence of a complex decomposition mechanism.

In addition to the two iso-conversional methods we have also used the Kissinger method for calculating a single value of parameter *E*. The closeness of this value to the estimates of those obtained from iso-conversional methods gives some support to use the kinetic analysis results for further calculations.

FOX-7

For FOX-7 the results of the three above-mentioned methods are given in Table 3.

The results are in close agreement, and give results which are close to those found when analysing single curves. The plot of the parameter *E*, calculated from iso-conversional methods, *vs.* conversion shows a quite constant value from 0.2 to 0.8 conversion (Fig. 6). This gives support to the assumption that there is a single process occurring during the heating of FOX-7. If *E* would depend on conversion, this would be an indication of sequences of reactions, rather than a single reaction.

Table 3 Results of the kinetic studies on FOX-7, evaluated according to the Kissinger, modified Flynn–Wall–Ozawa and the Friedmann method

	Kissinger method	Integral iso-conversional method	Differential iso-conversional method
E/kJ mol^{-1}	372.3	326±28.7	334.5±22.9
ln$A$/s^{-1}	–	79.802±6.905	80.912±5.888
n	–	0.7	0.7

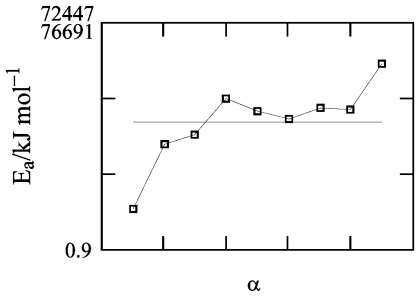


Fig. 6 Calculated activation energies as function of the converison (The horizontal line is the average)

These results indicate that a single reaction is occurring for this decomposition process. The averaged kinetic parameters characterising the decomposition process of FOX-7 are:

E=338.8 kJ mol^{-1} A=1.266·10^{38} s^{-1} n=0.7 (close to 2/3!)

These kinetic parameters can be used to reconstruct the original TG and DTA curves, Fig. 7. These reconstructed curves are in good agreement with the measured ones, implying that the kinetic parameters describe the decomposition reaction of FOX-7 reasonably well.

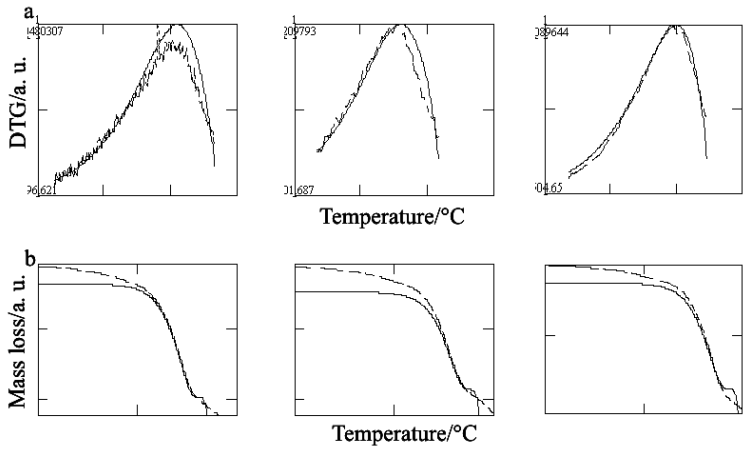


Fig. 7 Comparison between the experimental data of FOX-7 (TG/DTA) and the theoretical calculations using the kinetic parameters E, n and A. The continuous lines represent the theoretical calculations and the broken ones refer to the experimental data

Based on these parameters one can calculate the 'life time' of the sample when stored at temperature T_s. The equation below allows calculating the time in seconds until a fraction α of the FOX-7 has been converted (decomposed) into other products at temperature T_s:

$$t = \frac{1-(1-\alpha)^{1-0.7}}{(1-0.7)\,A\exp(-E/RT_s)}$$

where R is the gas constant (8.31 J K mol^{-1}), and A and E are the values of the pre-exponential factor and activation energy, respectively, as given above.

A simple calculation shows that storage temperatures in the range of 90–95°C lead to ~10 years for 10% conversion (α=0.1), while a temperature of 100°C results in about one year for decomposing the same 10%.

The value of 0.7 obtained for the reaction order should be interpreted only in relation with other structural investigations. At first sight the value is close to 2/3, as it is theoretically predicted for a phase boundary reaction with spherical symmetry. But no speculations can be done further, without knowledge of the chemistry of the process and e.g. X-ray results giving information about the existence of other crystalline phases.

HNF

Due to the influence of thermal effects, shifts and overlapping of the measured curves were found. For this reason, the integral iso-conversional method (i.e. the modified Flynn–Wall–Ozawa method) gives poor statistical results and has not been used during this analysis. The Friedmann method is used for each heating rate, as well as for the whole group, and Kissinger method for the shifting of peak temperatures. The results are summarised in Table 4.

Table 4 Results of the kinetic studies on HNF, evaluated on the basis of the Kissinger and Friedmann method

HR/K min^{-1}	2.5	5	7.5	10	Differential iso-conversional	Kissinger
E/kJ mol^{-1}	222.9	255.3	209.9	217.9	225.0±12.6	234.7
n	1	1	1	1	1	–
ln*A*	67.385	76.748	62.662	65.167	67.826±3.325	–

The results are in a satisfactory agreement with each other. The four plots seem to be well described by a first-order reaction with an activation energy of E=226.5 ±17.26 kJ mol^{-1} and ln$A$=67.99±5.325 min^{-1}, in a close agreement with the values obtained by differential iso-conversional and Kissinger methods respectively. The plot

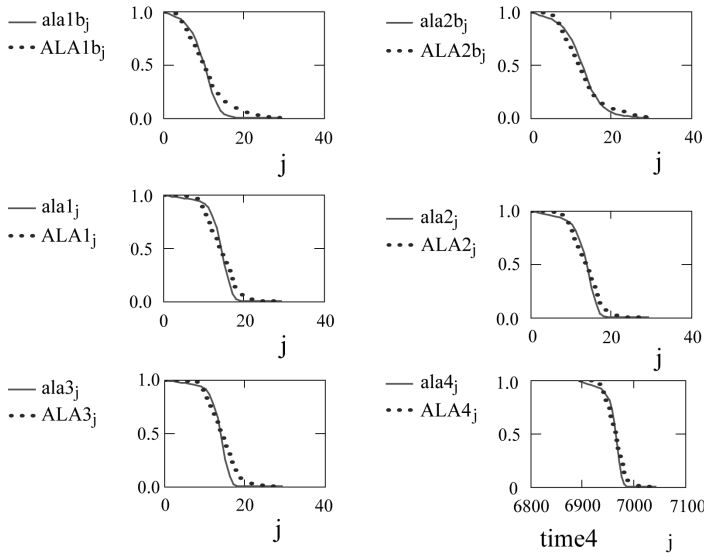


Fig. 8 Reconstruction of TG curves (line – reconstructed; dotted – original). In these graphs 'ala1b' refers to a relatively low mass sample at 5 K min^{-1}, 'ala2b' is a low mass sample at 10 K min^{-1}, 'ala1', 'ala2', 'ala3' and 'ala4' represent the relatively large mass samples at 2.5, 5, 7.5 and 10 K min^{-1}, respectively

of parameter E, calculated from differential iso-conversional method, *vs.* conversion degree does not support a complex mechanism for decomposition.

Thus it may be concluded that there is a single reaction occurring for this decomposition process. The averaged kinetic parameters for the process are:

E=226.2 kJ mol^{-1} A=5.44·10^{27} s^{-1} n=1

These kinetic parameters can be used to reconstruct the TG and DTA curves of HNF, Fig. 8. This reconstruction shows that the measured data can be fitted reasonably well.

Lifetime prediction

Similar to FOX-7, also for HNF a 'lifetime' of the sample when stored at temperature T_s can be calculated, using the same general equation as mentioned previously.

A plot of the 'lifetime' *vs.* the temperature is shown in Fig. 9. The two lines are

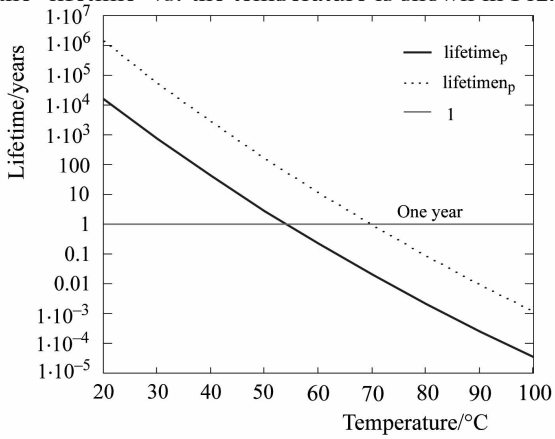


Fig. 9 Lifetime prediction

the limits calculated when taking into account the standard deviations of the values of the pre-exponential factor and the activation energy. The time scale is the logarithm of the storage period in years. One may notice that the product is very sensitive to storage temperatures above 50°C: storing it close to this temperature, the sample will show a conversion (decomposition) of about 10% in less than one year. This is in line with the practical experience with HNF: in general it is advised not to exceed temperatures of 60°C when storing and handling HNF, either separately or in combination with other materials. Temperatures of 40°C are very well possible, e.g. for curing propellants or for temporary storage.

Conclusions

The energetic materials FOX-7 and HNF have been subjected to TG/DTA studies, including a kinetic analysis, in order to obtain more insight into the decomposition kinetics of these two energetic materials. For FOX-7 evidence has been found for the occurrence of phase transitions, in agreement with other work [5]. For both FOX-7 and HNF the results support a single decomposition reaction, rather than a complex decomposition mechanism. The decomposition reactions of FOX-7 and HNF have been described with three parameters: the activation energy (E), a pre-exponential factor (A) and the reaction order (n). A reasonable agreement has been found between the reconstruction of the TG/DTA curves using the values of these calculated parameters and the experimental data. Moreover, these parameters allow a prediction of the lifetime of FOX-7 and HNF when stored at a certain temperature.

* * *

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