



Stability Analysis of n-Butyl-nitratoethylnitramine (Bu-NENA)

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Abstract: This article describes the thermal decomposition of n-Butyl-nitratoethylnitramine (Bu-NENA) which is a relatively new, not very widely used energetic plasticizer having attractive features. The decomposition reaction is a hydrolysis which leads to the formation of n-Butyl-ethanolnitramine (Bu-ENA) and nitric acid. The stability of Bu-NENA can be measured by the Bu-ENA formation rate and by microcalorimetry. The stability of high quality material is good enough that a stabilizer is not necessarily needed. As the main reaction is forced by hydrolysis it is recommended that Bu-NENA is stored in dry conditions. Surprisingly DSC does not differentiate very well between stable and unstable samples. The main difference is found in the peak areas, not in the onset or peak maximum temperatures. The decomposition product Bu-ENA is still an energetic material with an exothermic decomposition behaviour.

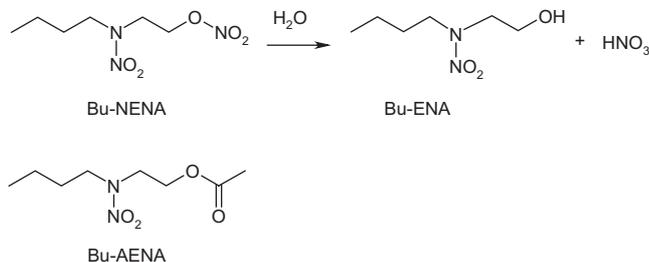
Keywords: energetic plasticizer, decomposition, kinetics, microcalorimetry, HPLC, DSC, moisture effect

Introduction

n-Butyl-nitratoethylnitramine (Bu-NENA) is a relatively new, not very widely used energetic plasticizer which has attractive features. It combines properties of nitrate esters and nitramines and is a suitable plasticizer for gun and rocket propellants. It is even in discussion to replace carcinogenic dinitrotoluenes in gun propellants. At least developments are underway to formulate Bu-NENA plasticized propellants on HTPE (hydroxyterminated polyethers) basis with full IM properties [1].

It has one nitrate ester group and one nitramine group in its molecular structure. If stability and sensitivity of Bu-NENA are compared with trinitroglycerin (NG), Bu-NENA shows a much higher stability and lower sensitivity, but as all nitrate esters it suffers from an inherent instability due to the low O-NO₂ bond energy [2]. This bond can either be split homolytically (radical formation and subsequent reactions) or hydrolytically (formation of nitric acid and the corresponding alcohol Bu-ENA). The Bu-ENA formation reaction during ageing is shown in Scheme 1, which also shows the structural formula of Bu-AENA, a precursor molecule of Bu-NENA during production.

This work was done during the development of STANAG 4583, Edition 1 [3]. The aim was to find a suitable stability and quality test method for this new energetic plasticizer. We have performed chemical and thermal analyses with 9 different Bu-NENA batches from three different producers. All samples are listed in Table 1. The main interest was focussed on the chemical degradation of Bu-NENA to Bu-ENA and to the thermal analysis of different Bu-NENA batches (microcalorimetry [MC] and differential scanning calorimetry [DSC]).



Scheme 1. Structural formulae of Bu-NENA, Bu-ENA and Bu-AENA.

Materials

Table 1. Sample list

Sample name ^{c)}	Age [y]	Stabilizer	Bu-NENA content [%]	Bu-AENA ^{d)} content [%]	Bu-ENA ^{e)} content [%]	Moisture content [%] ^{b)}
Bu-NENA Nr. 1	1	MNA ^{a)}	97.0	0.49	0.053	0.13
Bu-NENA Nr. 2	1	MNA ^{a)}	96.0	0.46	0.040	0.12
Bu-NENA Nr. 3	1	none	97.2	0.20	0.043	0.13
Bu-NENA Nr. 4	1	none	97.0	0.44	0.059	0.12
Bu-NENA Nr. 10	0.5	none	96.6	0.38	0.031	0.09
Bu-NENA Nr. 11	0.5	none	97.4	0.39	0.047	0.09
Bu-NENA 603/05	0.1	none	96.0	0.49	0.040	0.065
Bu-NENA B	ca 8	none	82.0	1.30	1.50	1.2
Bu-NENA RXL647	10	none	93.2	2.38	0.32	0.19

a) MNA = p-nitro-*N*-methyl aniline

b) The moisture content was measured long after reception of the samples, so it does not reflect the original moisture content. Nevertheless, it clearly divides ‘wet’ from ‘dry’ sample types
As Bu-NENA is hygroscopic, it is recommended to store it in closed, moisture-free bottles

c) The samples from Nr. 1 to 603/05 were produced in one company, Bu-NENA B was purchased from a second factory, and the RXL material came from a third producer

d) Bu-AENA = *N*-n-butyl-*N*-nitro-2-aminoethanol-1-acetate (see Scheme 2)

e) Bu-ENA = *N*-n-butyl-*N*-nitro-2-aminoethanol (see Scheme 2)

Two of the samples were MNA stabilized (MNA is the usual stabilizer for this energetic plasticizer). The Bu-AENA level of the first seven samples is very low, according to type 1 or 3 of STANAG 4583. The Bu-NENA sample from company B has been less well stored in the past years, and self-decomposition has already started. This is visible by its dark brown colour and its high Bu-ENA content. This sample also showed an extraordinary high moisture level (STANAG 4583, Ed. 1 limits this value to 0.05%). The last sample from company C had a much higher Bu-AENA content than all the others. Its moisture level is also beyond the STANAG specification.

For some experiments additional samples were taken. They are listed in the respective part of the text.

Methods

High performance liquid chromatography (HPLC)

HPLC measurements were performed using a Gynkotek HPLC system with UV/DAD detection under following conditions: Column: Lichrospher 100 RP 18.5 μm , 250/20/4 mm, solvent: acetonitrile/methanol/water 20:40:40 (v/v), flow rate: 0.8 ml min⁻¹, temperature: 15 °C, detection wavelength: 225 nm. Under these conditions a baseline separation of Bu-NENA, Bu-AENA and Bu-ENA as well as MNA and its *N*-nitroso derivative (*N*-NO-MNA = *N*-nitroso-*N*-methyl-4-nitroaniline) was possible.

Karl Fischer titration

The samples were titrated after dissolution in dry methanol according to German TL procedure [4]. The indication occurred coulometrically. The titer of the solvent was determined under identical conditions.

Acidity

Acidity was determined by titration as described in STANAG 4583 (Test 1) [3].

Microcalorimetry (MC)

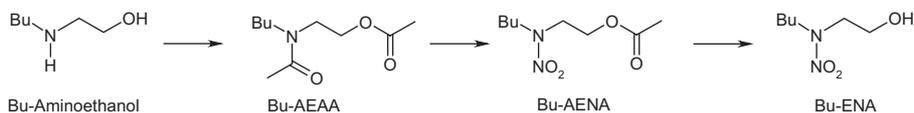
The 3 ml glass vials were 2/3 filled with Bu-NENA and then crimped in order to obtain an airtight seal. Microcalorimetric measurements were conducted with a TAM III or a TAM 2277 microcalorimeter (Thermometric AB, Järfälla, Sweden) at temperatures of 80 °C (all samples). Additional measurements were performed at 70 °C and 89 °C to determine the activation energy (iso α evaluation).

Differential scanning calorimetry (DSC)

DSC experiments were conducted in closed pressure crucibles (unless otherwise stated) either dynamically (preferred heating rate 2 K/min) or isothermally. All experiments were performed in a simultaneous DSC/TG apparatus STA 429 (Netzsch GmbH, Selb, Germany).

Synthesis of Bu-AENA and Bu-ENA

The compounds were synthesized according to literature procedures [5, 6]. The following scheme shows the reaction pathway.



Scheme 2. Synthetic route to Bu-AENA and Bu-ENA.

The reaction to Bu-AEAA is an acetylation reaction [6] which was proceeded in acetic anhydride. Bu-AEAA is nitrated in trifluoroacetic anhydride with concentrated nitric acid at $-5\text{ }^{\circ}\text{C}$ [6]. The hydrolysis of Bu-AENA to Bu-ENA occurs in 2M HCl over night at $80\text{ }^{\circ}\text{C}$ [6]. The overall yield of this reaction is about 40%.

The identity and purity of the products was checked by elemental analysis, mass spectrometry, HPLC and by ^1H and ^{13}C NMR spectroscopy.

Ageing of samples

Samples Bu-NENA 2, Bu-NENA 4, Bu-NENA 603/05, Bu-NENA B and Bu-NENA RXL 647 were aged at $70 \pm 0.5\text{ }^{\circ}\text{C}$ and at $90 \pm 0.5\text{ }^{\circ}\text{C}$ in 2/3 filled and sealed microcalorimetry ampoules. Interestingly, most of the samples became brighter during ageing. The temperature/time scheme is presented in Table 2.

Table 2. Ageing of different Bu-NENA charges (time in days)

Sample	T [°C]	Ageing [d]
Bu-NENA Nr. 2	70	10.3, 32.0, 33.0, 63.0, 106, 141
Bu-NENA Nr. 2	90	2.0, 4.0, 7.0, 14.0, 23.0
Bu-NENA Nr. 4	70	10.3, 24.0, 33.0, 63.0, 106
Bu-NENA Nr. 4	90	2.0, 7.0, 14.0, 22.0
Bu-NENA 603/05	70	10.3, 21.3, 33.0, 47.0, 80.0, 106, 141, 154
Bu-NENA 603/05	90	2.0, 4.1, 7.0, 10.3, 14.0, 18.2, 23.0, 28.0
Bu-NENA B	70	10.3, 33.0, 63.0, 109
Bu-NENA B	90	2.1, 4.2, 7.0, 14.0, 22.0, 27.0
Bu-NENA RXL 647	70	10.3, 21.0, 22.0, 47.0, 80.0
Bu-NENA RXL 647	90	2.1, 4.2, 7.0, 14.0, 18.0, 28.0, 33.0

In addition samples in 1/10 filled ampoules, after addition of small amounts (around 4 wt%) of water, diluted acid (0.01 M HCl) and diluted base (0.01 M NaOH) and after addition of akardite II were aged.

After ageing the sample ampoules were opened and around 100 mg of the sample was diluted in methanol and used for chromatographic examination.

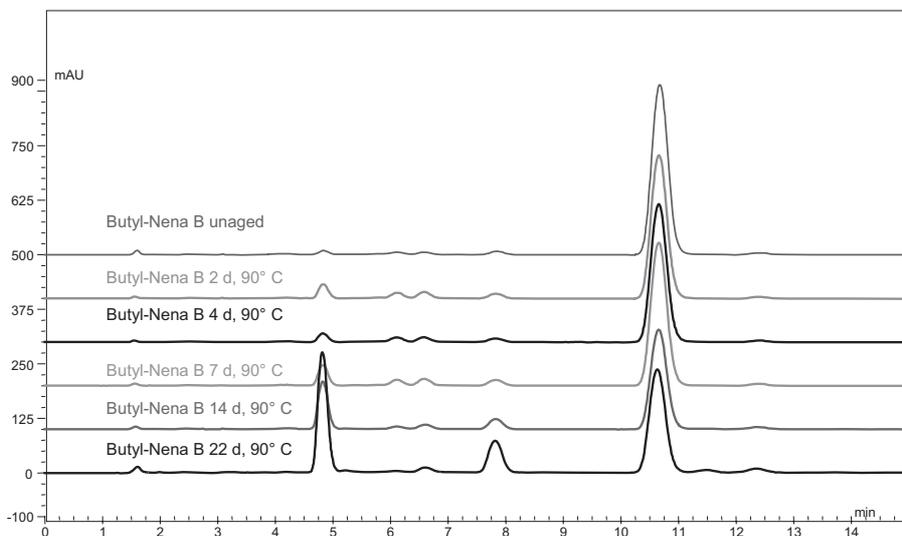


Figure 1. Chromatograms of Bu-NENA before and after ageing. Bu-NENA appears at about 11 mins, Bu-ENA elutes after around 5 mins. The peak at 8 mins refers to Bu-AENA.

Results

Bu-NENA depletion / Bu-ENA formation

A typical chromatogram is presented in Figure 1. A base line separation (even if MNA and *N*-NO-MNA are present) could be achieved. In the waterfall plot the increase of Bu-ENA and the decrease of Bu-NENA is clearly visible. In this case also Bu-AENA content increases, this is mainly due to a massive weight loss during ageing of this unstable sample.

'Normal' conditions

The results of this study are collected in the following tables. The large number of experimental data made a selection of the most important values necessary. Table 3 includes the MNA and *N*-NO-MNA content of the stabilized sample Nr. 2. The Bu-AENA content does not change significantly throughout the ageing of the material (exception: Bu-NENA sample B). Therefore this compound is not mentioned in the following tables.

Table 3. HPLC results after ageing at 90 °C. All values in wt%

t	NENA Nr. 2				NENA Nr. 4		NENA 603/05		NENA B		NENA RXL	
[d]	NENA	ENA	MNA	NNO	NENA	ENA	NENA	ENA	NENA	ENA	NENA	ENA
0	96.0	0.04	0.52	0.00	97.0	0.06	96.0	0.04	86.0	1.50	93.2	0.32
2	96.0	0.16	0.20	0.27	96.3	0.16	95.5	0.10	79.6	3.92	92.1	0.80
4	96.2	0.20	0.00	0.47	-	-	95.4	0.22	75.2	5.90	90.8	1.24
7	93.0	0.44	0.00	0.46	95.5	0.46	95.3	0.36	72.5	8.41	89.5	1.89
10	-	-	-	-	-	-	95.1	0.59	-	-	88.4	2.61
14	92.8	1.04	0.00	0.47	93.9	0.90	94.2	0.83	55.1	21.8	88.3	3.27
18	-	-	-	-	-	-	93.5	1.23	-	-	85.9	4.13
23	92.1	1.95	0.00	0.44	94.9 ^{a)}	1.69 ^{a)}	91.6	1.91	33.5 ^{a)}	31.2 ^{a)}	-	-
28	-	-	-	-	-	-	90.7	2.13	26.2 ^{b)}	38.1 ^{b)}	81.4	6.39

a) sample aged for 22 days

b) sample aged for 27 days

Abbreviations: NENA = Bu-NENA, ENA = Bu-ENA, NNO = N-NO-MNA, - = not measured

Table 4. HPLC results after ageing at 70 °C. All values in wt%

t	NENA Nr. 2				NENA Nr. 4		NENA 603/05		NENA B		NENA RXL	
[d]	NENA	ENA	MNA	NNO	NENA	ENA	NENA	ENA	NENA	ENA	NENA	ENA
0	96.0	0.04	0.52	0.00	97.0	0.06	96.0	0.04	86.0	1.50	93.2	0.32
10	95.4	0.13	0.31	0.08	92.5	0.13	95.9	0.09	75.9	3.64	92.2	0.57
21	-	-	-	-	96.0 ^{a)}	0.18 ^{a)}	95.6	0.16	-	-	90.3	0.76
33	94.6	0.17	0.21	0.23	93.4	0.32	95.5	0.26	75.0	6.36	-	-
47	-	-	-	-	-	-	93.5	0.34	-	-	93.0	1.53
63	95.1	0.23	0.00	0.40	95.1	0.37	-	-	69.8	10.9	-	-
80	-	-	-	-	-	-	95.5	0.40	-	-	-	-
106	94.8	0.47	0.00	0.47	95.2	0.65	95.2	0.64	59.4	14.9	-	-
141	96.0	0.68	0.00	0.41	-	-	96.4	0.69	-	-	-	-

a) sample aged for 24 days

Abbreviations: NENA = Bu-NENA, ENA = Bu-ENA, NNO = N-NO-MNA, - = not measured

Wet' conditions

These experiments were only conducted with samples Bu-NENA Nr. 2 and 603/05. Table 5 shows the results of HPLC after ageing.

Table 5. Results of HPLC analyses of sample Bu-NENA 2 after ageing under wet, acidic and basic conditions

t	Addition of water				Addition of acid				Addition of base			
	NENA	ENA	MNA	NNO	NENA	ENA	MNA	NNO	NENA	ENA	MNA	NNO
[d]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]
0	96.02	0.04	0.52	0.00	96.02	0.04	0.52	0.00	96.02	0.04	0.52	0.00
2	90.49	0.77	0.00	0.40	92.59	0.73	0.00	0.29	93.52	0.80	0.00	0.56
4	89.18	1.96	0.00	0.27	87.53	1.76	0.00	0.27	91.94	1.31	0.00	0.29
7	87.58	3.84	0.00	0.29	89.65	3.67	0.00	0.29	90.25	3.58	0.00	0.25

Abbreviations: NENA = Bu-NENA, ENA = Bu-ENA, NNO = N-NO-MNA

Sample 603/05 shows a very similar behaviour. After 7 days the Bu-NENA concentration falls to 84-85%, whereas the Bu-ENA content increases to about 6-7%. So the changes are even more drastic than in the case of stabilized sample Bu-NENA Nr. 2.

Additional experiments

To study the oxygen dependence of the reaction samples of Bu-NENA Nr. 2 and Bu-NENA 603/05 was aged in only a 1/10 filled and sealed 3 mL glass ampoule. Table 6 shows the results of the HPLC analysis after ageing in comparison with data gathered from full ampoule ageing.

Table 6. Comparison of HPLC data after ageing in full (2/3 filled) ampoules and low LD (1/10 filled) conditions

t	Sample Bu-NENA Nr. 2 low LD				Sample Bu-NENA Nr. 2 filled				Sample Bu-NENA Nr. 603/05 low LD		Sample Bu-NENA Nr. 603/05 filled	
	NENA	ENA	MNA	NNO	NENA	ENA	MNA	NNO	NENA	ENA	NENA	ENA
[d]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]
0	96.0	0.04	0.52	0.00	96.0	0.04	0.52	0.00	96.0	0.04	96.0	0.04
2	93.8	0.14	0.12	0.23	96.0	0.16	0.20	0.27	95.0	0.09	95.5	0.10
4	89.5	0.15	0.00	0.33	96.2	0.20	0.00	0.47	93.0	0.19	95.4	0.22
7	92.4	0.26	0.00	0.30	93.0	0.44	0.00	0.46	94.1	0.26	95.3	0.36

Abbreviations: NENA = Bu-NENA, ENA = Bu-ENA, NNO = N-NO-MNA

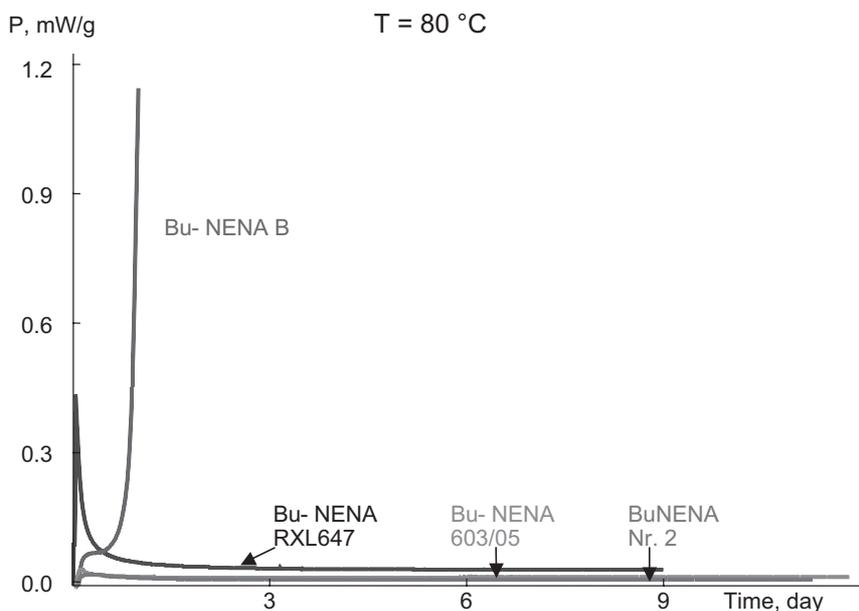
Table 7. Bu-NENA depletion (sample 603/05) at 90 °C (stabilized with Ak II)

t	Bu-NENA	Bu-ENA	Ak II	2,4'-DNDPA	2,2',4-TNDPA	2,4,4'-TNDPA	2,2',4,4'-TeNDPA
[d]	[%]	[%]	[%]	[%]	[%]	[%]	[%]
0	95.1	0.00	0.87	0.00	0.00	0.00	0.00
4	94.9	0.44	0.79	0.00	0.00	0.09	0.00
7	94.8	0.73	0.54	0.06	0.00	0.16	0.00
13	91.9	1.81	0.30	0.05	0.00	0.35	0.00
22	89.4	2.35	0.30	0.00	0.20	0.31	0.45

Abbreviations: Ak II = akardite II, DNDPA = dinitrodiphenylamine, TNDPA = trinitrodiphenylamine, TeNDPA = tetranitrodiphenylamine

Microcalorimetry

Microcalorimetric experiments were performed at 80 °C and at 89 °C with most of the samples. The following figures show the most relevant experiments.

**Figure 2.** Measurement of Bu-NENA samples at 80 °C.

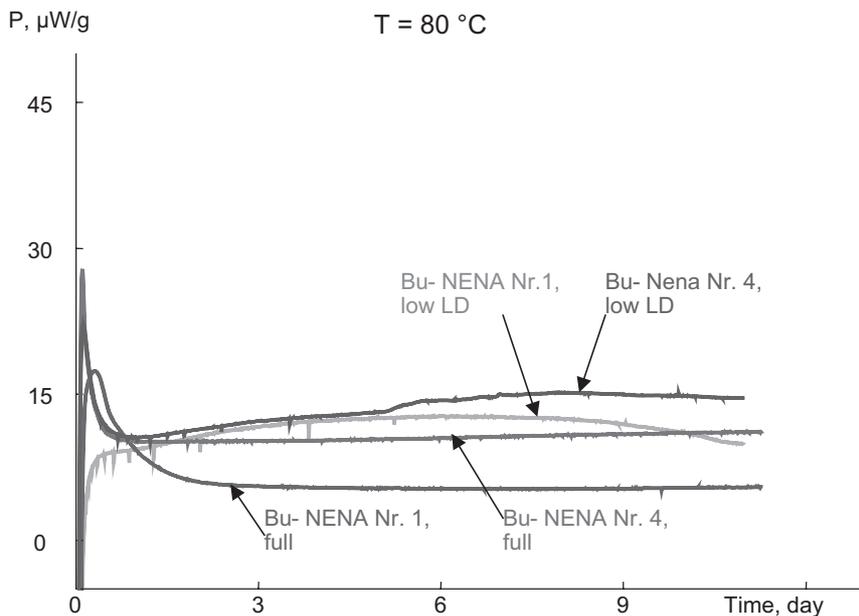


Figure 3. Comparison of samples #1 and #4 (full ampoule and reduced loading density).

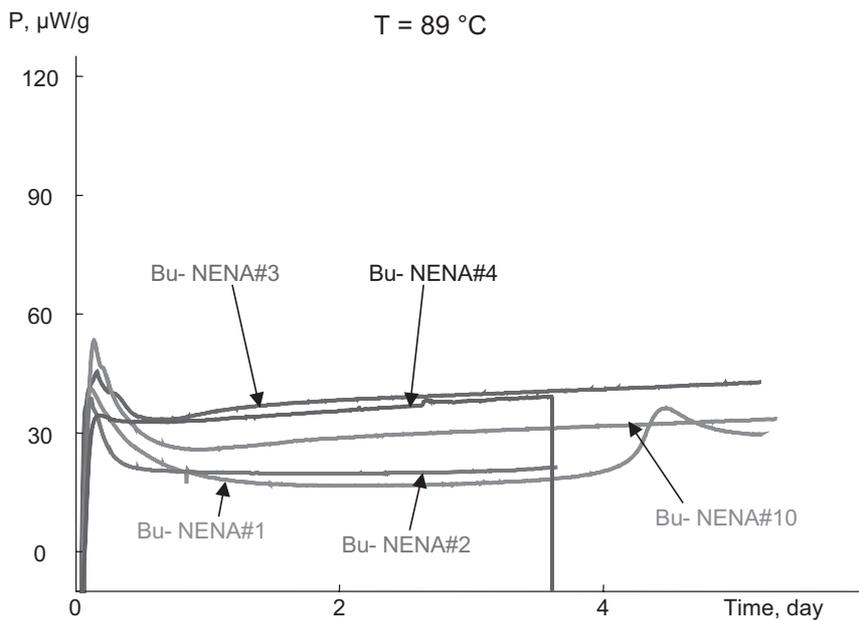


Figure 4. Measurement of Bu-NENA samples at 89 °C.

Differential scanning calorimetry

Table 8 shows the experiments that were conducted to identify the dependence of the DSC signal on the measuring conditions and the Bu-NENA sample type. Fresh samples Bu-NENA Nr. 1, Bu-NENA Nr. 3, Bu-NENA RXL647, Bu-NENA B and Bu-NENA B after pre-ageing of 105 d at 70 °C were investigated dynamically ($H = 2$ K/min) and isothermally (150 °C). All experiments (except for one) were performed in hermetically sealed DSC pressure crucibles. In addition Bu-AENA and Bu-ENA were tested dynamically. The following figures show the relevant results.

Table 8. Summary of DSC experiments with different Bu-NENA samples

Probe	Q [J/g] at 150 °C	T_{onset} [°C] at 2 K/min	Q [J/g] at 2 K/min, sealed crucible	Q [J/g] at 2 K/min, open crucible
Bu-NENA Nr. 1	2682	176.0	2806 ¹⁾	n.p.
Bu-NENA Nr. 3	2703	176.4	3024 ¹⁾	n.p.
Bu-NENA RXL 647	2112	173.4	2424 ¹⁾	239 ¹⁾
Bu-NENA B	1861	175.4	2059 ¹⁾	n.p.
Bu-NENA B, 106 d 70 °C	n.p.	174.6	1458 ¹⁾	n.p.
Bu-AENA	n.p.	239.8	1354	n.p.
Bu-ENA	n.p.	244.0	1561	n.p.

n.p. = not performed

1) for the first part reaction (below 220 °C)

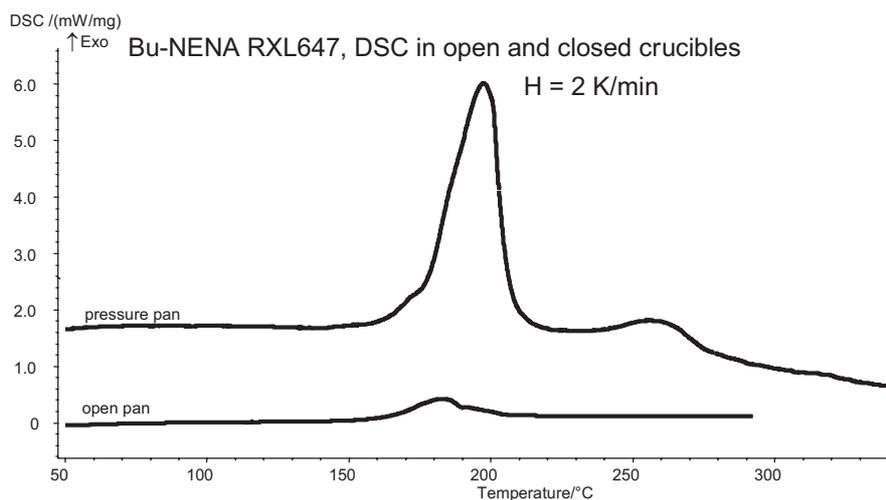


Figure 5. Comparison of a measurement in closed (pressure) and open crucibles.

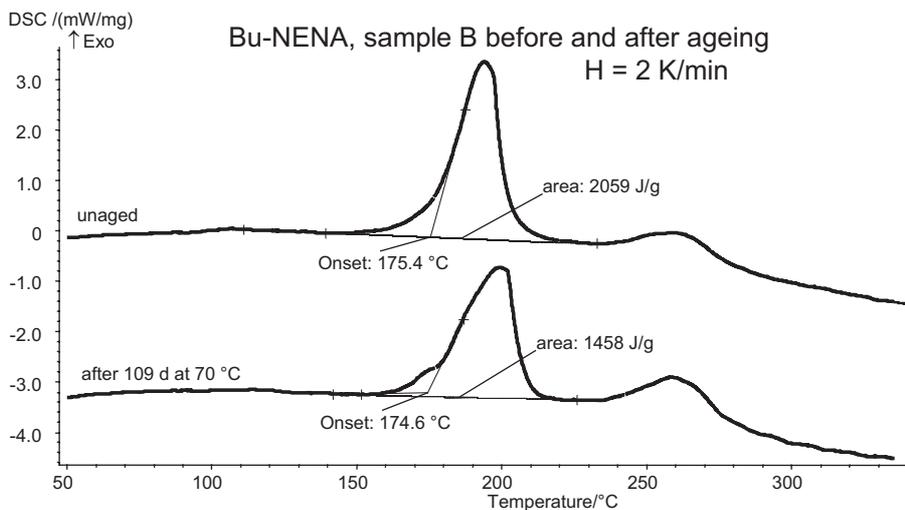


Figure 6. Comparison between unaged and aged sample (Bu-NENA B).

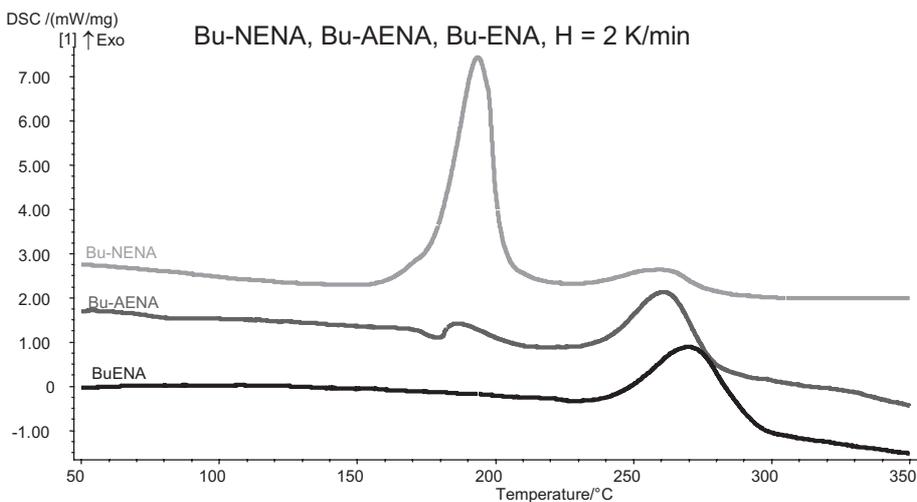


Figure 7. Thermograms of Bu-NENA, Bu-AENA and Bu-ENA.

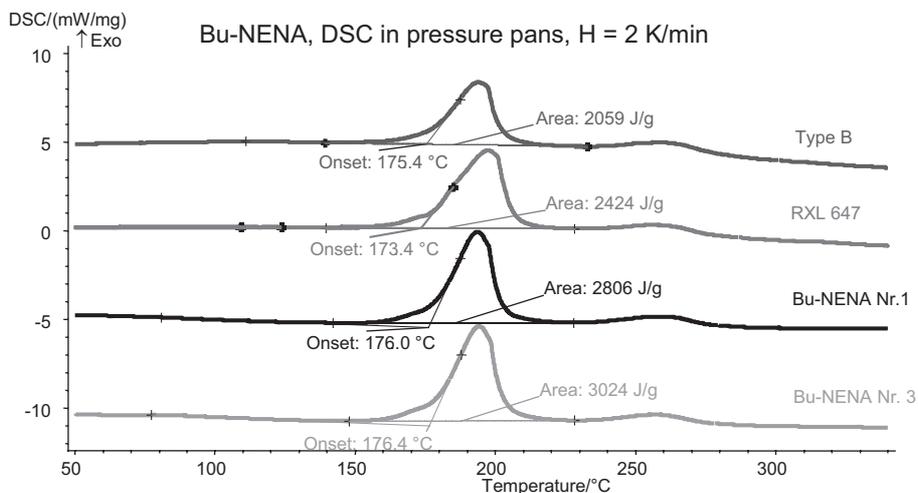


Figure 8. Comparison between four different Bu-NENA samples (dynamic experiment in sealed pressure crucibles, H = 2 K/min).

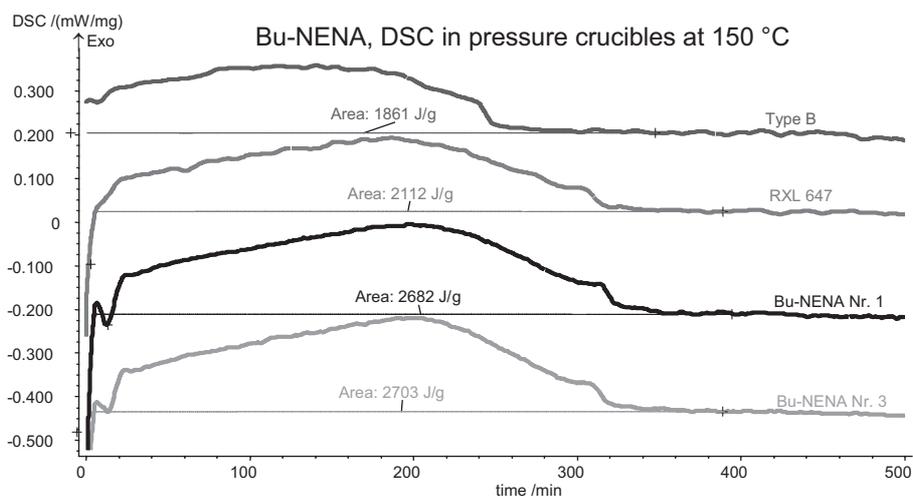


Figure 9. Comparison between four different Bu-NENA samples (isothermal experiment in sealed pressure crucibles, T = 150 °C).

Wet chemistry

A long-term pH study was undertaken in one of the producer's laboratories. A slow but constant increase of acidity of three batches, produced in the year 2000, could be observed. Figure 10 shows the graph.

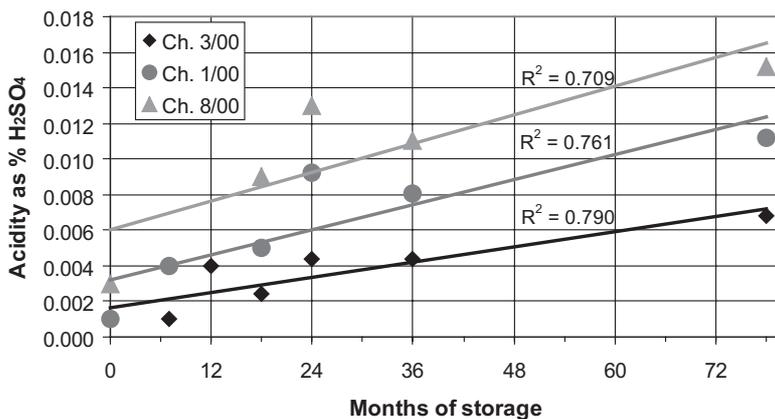


Figure 10. Increase of acidity during storage at ambient conditions.

Discussion

Bu-NENA depletion / Bu-ENA formation

As in general, HPLC determinations of purity based on the main component, like Bu-NENA here, are more difficult than HPLC analyses of impurities in a low percentage level. Therefore the Bu-NENA concentrations suffer from scattering much more than those of Bu-ENA. Nevertheless, a clear discrimination between 'stable' and 'less stable' substances can be drawn from the Bu-NENA depletion data.

These depletion data correspond with the Bu-ENA formation rate. Figures 11a and 11b show the correlation between the concentration change of these two compounds.

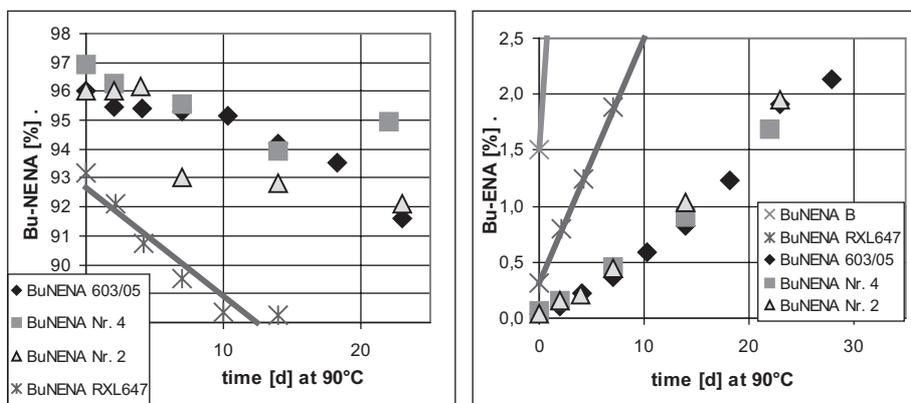


Figure 11a. Bu-NENA depletion (left) and Bu-ENA formation (right) of various samples at 90 °C.

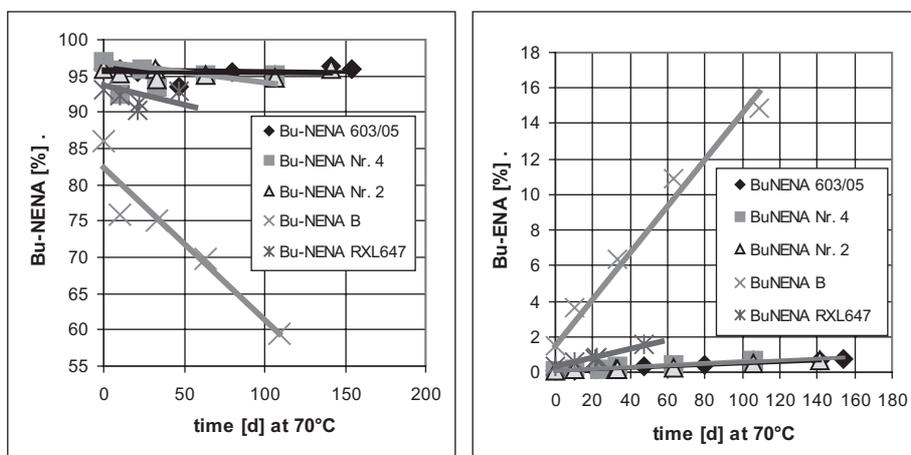


Figure 11b. Bu-NENA depletion (left) and Bu-ENA formation (right) of various samples at 70 °C.

If one looks carefully at the graphs, a slightly autocatalytic behaviour can be detected, so a straight line with a constant slope does not fit the data perfectly. Nevertheless, this graph can be used for a comparative evaluation and for a basic kinetic assessment of the Bu-ENA formation rate and the Bu-NENA depletion rate (see Table 9).

Table 9. Slopes of Bu-NENA depletion and Bu-ENA formation (assuming a 0 order reaction) of different Bu-NENA samples

Sample	T [°C]	Nr. 2	Nr. 4	603/05	B	RXL647
depletion Bu-NENA [%/d]	90	-0.221	-0.133	-0.184	-2.252	-0.377
formation Bu-ENA [%/d]	90	0.078	0.069	0.071	1.350	0.216
depletion Bu-NENA [%/d]	70	-0.012	-0.029	-0.034	-0.210	-0.055
formation Bu-ENA [%/d]	70	0.0042	0.0056	0.0049	0.131	0.025

MNA depletion

MNA is a very reactive stabilizer [7]. It is consumed extremely rapidly compared to other usual stabilizers. Its reaction product is the highly carcinogenic N-NO-MNA which itself is only very slowly consumed. The time of complete MNA consumption corresponds to a second maximum in heat generation (see e.g. in Figure 4 the curve of Bu-NENA Nr. 1 after 4.5 days, see also Figure 12 for a correlation between released energy and MNA depletion). MNA is depleted faster in presence of moisture. This is the case because S_N reactions produce much more HNO_3 due to hydrolysis which nitrosates the stabilizer faster. Even in higher aged samples no trace of dinitro-MNA or its nitroso compound could be identified. This is consistent with the nearly constant level of N-NO-MNA after complete MNA consumption.

The comparison of stabilized and unstabilized Bu-NENA clearly shows that this only slightly unstable material does not need a stabilizer in general. Therefore it is recommended to produce Bu-NENA without stabilizer and to keep it away from moisture. Then a long-term stability at ambient temperatures can be guaranteed.

Microcalorimetry

The microcalorimetric curves differ between stabilized and unstabilized samples. The stabilized samples have a first minimum until the end of the 3rd day at 89 °C (see Figure 4). Then an increase occurs which corresponds to the complete consumption of MNA. This ‘second maximum’ is analogous to that found in DPA stabilized samples [8]. Unstabilized material shows a constantly slightly increasing generation rate at a very moderate level (if compared with propellants or other liquid nitrate esters [9]), which make them all fit the limit values of STANAG 4582 [10]. Only the ‘lower quality’ samples (RXL 647 and sample B) have a much higher heat generation rate, the latter sample rapidly increasing into an autocatalysis after 1 day at 80 °C (see Figure 2).

There is a good correlation between stabilizer depletion, Bu-ENA formation and released energy as depicted in Figure 12, independent from the ageing temperature.

The difference between samples in 2/3 filled ampoules and measurements with a very low loading density is rather small. This underlines the small influence of atmospheric oxygen on the ageing reaction mechanism (see Figure 3).

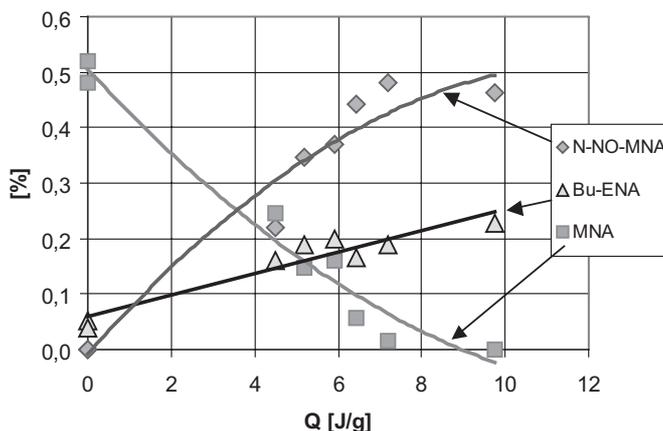


Figure 12. Correlation between stabilizer depletion, Bu-ENA formation and energy release (microcalorimetry, $T = 70, 80$ and 89 °C, samples Bu-NENA Nr. 1 and Nr. 2).

DSC

DSC has to be performed in completely closed pressure DSC crucibles. Otherwise evaporation will cause wrong results.

DSC is not a good method to differentiate between stable and unstable samples, independent if one looks at onset or peak maximum temperatures (differences are about 1-2 °C, too small to generalize them exactly in a STANAG). The only thing what is significantly different are the peak areas. Bad lots have definitely smaller decomposition heats than good lots if samples without Bu-AENA are compared. However, also stable samples containing Bu-AENA (according to STANAG 4583 type 2 and 4 Bu-NENAs may contain up to 8% Bu-AENA) would give lower first peak decomposition areas. A discrimination between stable, but Bu-AENA containing samples and unstable, Bu-ENA containing samples cannot be based solely on DSC, even if the sum of the first and the second peak area is considered. The main reason for this is the very similar decomposition characteristics of Bu-AENA and Bu-ENA (see Figure 7). In addition, the evaluation of the peak areas of type 2 and 4 NENAs may suffer

from a not-baseline-separated heat flow curve (Bu-AENA decomposition starts at 240 °C, just before the end of the Bu-NENA decomposition peak).

Kinetic evaluation

The kinetic evaluation of Bu-NENA samples was performed according to the method described in [11]. Table 10 contains the results of these calculations. Table 11 summarizes the activation energies for Bu-NENA depletion and Bu-ENA formation rates (values coming from Tables 3 and 4).

The scattering of data of Bu-NENA depletion rates is again much larger. This is due to the much smaller accuracy of the data. In contrast to that the data of the Bu-ENA formation rate are much closer to each other and they lie in the same range than the microcalorimetric values.

Table 10. Activation energies (iso- α evaluation) of different samples

Sample	α [J/g]	T range [°C] (T_1 - T_2)	Ea (P) [kJ/mole]	Ea (t) [kJ/mole]
Bu-NENA Nr. 2	4.5	89-70	148	135
Bu-NENA Nr. 3	11.2	89-80	127	125
Bu-NENA Nr. 4	10.7	89-70	109	104
Bu-NENA Nr. 10	5.5	89-80	142	132
Bu-NENA RXL647	27.5	89-80	117	123

Ea (P): activation energy calculated by using the ratio of heat flows at T_1/T_2 at α

Ea (t): activation energy calculated by using the ratio of times (t_2/t_1) to reach α

Table 11. Activation energies (Ea) from Bu-NENA depletion and Bu-ENA formation rates

Sample	T range [°C]	Ea (Bu-NENA depl.) [kJ/mole]	Ea (Bu-ENA form.) [kJ/mole]
Bu-NENA Nr. 2	90-70	114	151
Bu-NENA Nr. 4	90-70	73	130
Bu-NENA Nr. 603/05	90-70	86	139
Bu-NENA B	90-70	123	121
Bu-NENA RXL647	90-70	100	112

Influence of ageing conditions on the decomposition rate

In contrast to propellants the oxygen/sample ratio does not play a decisive role in ageing kinetics or reaction mechanisms. So neither the shape of the heat flow curve nor the composition of the depletion products nor the Bu-ENA formation rate differ much between the ‘normal’ and the ‘low loading density’ experiments.

Moisture is a very reactive partner in decomposition of Bu-NENA. The nitrate ester group is very sensitive to hydrolysis. It is unimportant whether acidic, neutral or basic conditions are present. The Bu-ENA formation rate is about 6-15 times higher than in the ‘normal’ case without addition of moisture. Table 12 contains all details.

Table 12. Bu-ENA formation rates under various conditions (values in %/day at 90 °C)

Condition	Bu-NENA Nr. 2	Bu-NENA 603/05
Normal conditions (2/3 filled ampoule)	0.054 ^{a)}	0.047 ^{a)}
Low loading density	0.029	0.033
Addition of H ₂ O	0.52	0.79
Addition of NaOH	0.45	0.91
Addition of HCl	0.49	1.03

a) values differ from those in Table 9, as for a better comparison only the first 7 days were evaluated here.

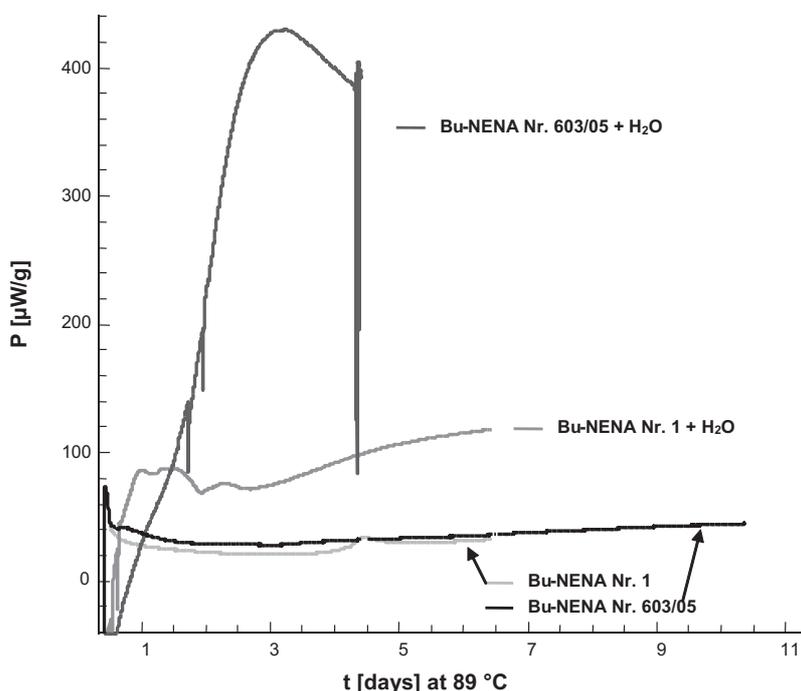


Figure 13. Comparison of dry and wet samples at 89 °C in a microcalorimetric experiment.

The higher decomposition rate is also clearly visible from Figure 13. The microcalorimetric experiments, conducted at 89 °C, show a significant difference between ‘normal’ (dry) and wet samples. The wet sample 603/05 has a higher heat generation rate, clearly missing the limit value of STANAG 4582 (314 $\mu\text{W/g}$) and ending shortly after the needed measuring time producing a huge gas evolution peak. Sample Bu-NENA Nr. 1 also has a higher heat generation rate than the dry sample, but the STANAG 4582 criteria are met.

Conclusion

The mixed nitrate ester and nitramine Bu-NENA is an energetic plasticizer with a moderate autocatalytic decomposition. It is much more stable than pure nitrate esters like nitroglycerin or diethyleneglycol dinitrate. Nevertheless, it decomposes slowly with time under formation of Bu-ENA. This reaction is rather a hydrolytic than a thermolytic decomposition. The reaction is accompanied by moderate heat generation, moderate gas production and an increase of acid concentration.

The reaction pathway to Bu-ENA was proven by synthesis of the decomposition product and by optimization of the chromatographic separation of all educts, by-products and stabilizers. No concurring reaction could be observed. Also there are no signs for a consecutive decomposition of Bu-ENA. Thermal analysis of Bu-ENA showed a higher stability of this compound which is still an energetic material.

The decomposition reaction can be speeded up by a factor of 6 to 15 by addition of small amounts (4 wt%) of moisture. In these cases a stabilizer can reduce this acceleration whereas under ‘normal’ conditions the formation rate of Bu-ENA is nearly identical to that of unstabilized samples. Therefore a stabilizer is not necessarily needed, and the use of MNA cannot be recommended, regarding the highly carcinogenic properties of its decomposition product N-NO-MNA. If a stabilizer is used, it is recommended to take Akardite II. No formation of N-NO-DPA was observed during artificial ageing of Akardite II stabilized Bu-NENA.

It is necessary to keep Bu-NENA away from moisture, then even unstabilized material is stable for decades at room temperature without any stabilizer.

Acknowledgements

This work was done in an excellent German-Norwegian cooperation. The authors wish to thank Anne Sommer (WIWEB) for HPLC analyses, Gabriele

Pantel (WIWEB) for microcalorimetric experiments, Dr. Uldis Ticmanis (WIWEB) for DSC analyses and intensive kinetic discussions, Katharina Klassen (Humboldt-Gymnasium Bornheim) for the preparation and ageing of the Bu-NENA samples, Roland Friedemann (FU Berlin) for the synthesis of Bu-AENA and Bu-ENA and his colleagues at FU Berlin for NMR measurements of the synthesized compounds.

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