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THE KINETIC BEHAVIOUR AND THERMAL STABILITY OF COMMERCIALLY AVAILABLE EXPLOSIVES

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Manufactures of commercially available explosives guarantee a certain lifetime of their products. In the commercial field this lifetime is usually large enough. The explosive is normally used long before the end of its lifetime. It may happen that these explosives are stored for a long time in a bunker where they sometimes exceed their lifetime.

A large set of commercial explosives is characterized with a TG by heating small samples in aluminium sample cups from room temperature to 550°C, under a nitrogen atmosphere, with three different heating rates (2, 5 and 10 K min^{-1}). The activation energy of the decomposition step is determined in several different ways. After this characterization, a selection of the samples (based on economical value) is artificially aged for periods of 2, 4 and 6 weeks. After these ageing profiles the samples are re-investigated with the TG under the same conditions (heating rates and atmosphere) followed by the calculation of the kinetic parameters of the artificially aged materials. According to the TG measurements almost all tested explosives appear to have a much longer lifetime than the values given by the manufacturer. From kinetic point of view, the different methods for calculating the activation energy result in approximately the same parameters. It may conclude that TG seems to be a reliable and quick method for the determination of the lifetime of commercial explosives.

***Keywords:** explosives, kinetic models, TG, thermal stability*

Introduction

The stability of propellants and energetic materials is one of the main topics studied in the research group pyrotechnics and energetic materials. In the research group different techniques are available for performing stability measurements. In this project thermogravimetric analysis (TG) is chosen because of the relatively short measurements (compared to e.g. heat flow calorimetry) and the availability of software for the kinetic calculations.

In the past TNO-PML has performed a lot of TG measurements on different types of energetic materials such as propellants, explosives, rocket compositions, etc. A new study is the investigation of the stability of commercially available explosives. Manufacturers of these kinds of explosives guarantee a relatively short lifetime for their products. In practice some of these explosives are stored for a long time in a bunker and they will exceed their lifetime. This project is used to find a method, which is quick and reliable, and can determine the lifetime of explosives.

Two different kinetic models have been used to determine the activation energy belonging to the decomposition process of the explosives. After ageing the samples, again the activation energy is determined. This may give an indication for the lifetime of the explosive.

The decomposition should keep the same kinetics independently of ageing, as a base of using the kinetic parameters for predictions. Beside, there is no chemical reason for which the kinetics would change only by storing a product.

Experimental

A Mettler Toledo TGA/SDTA 851^e 1600 LF/MT5 equipped with a robot is used for the TG measurements. Samples with a mass between 6.5 and 7.0 mg are placed in aluminium open sample cups with a volume of 40 μL. They are heated from room temperature to 550°C with three different heating rates (2, 5 and 10 K min^{-1}) under a nitrogen atmosphere (flow rate approx. 50 mL min^{-1}). The activation energy of the decomposition process is calculated with two different models.

The first model used is called 'model-free kinetics (MFK)'. This method is available in the STAR^e software of the Mettler Toledo equipment and is described in [1, 2].

The second kinetic model is a modified Kissinger equation which is described in [3–6].

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Model-free kinetics

MFK is based on the philosophy of Vyazovkin [1, 2] and the theory of Coats–Redfern, and applied by Mettler in the kinetic software. The theory is based on the assumption that

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = k\mathrm{e}^{-\frac{\mathrm{E}}{\mathrm{RT}}} f(\alpha) \tag{1}$$

and that the activation energy $E(\alpha)$ is constant for a certain conversion (α) (iso-conversion method). It is not necessary to choose a model before performing evaluation with MFK. The choice of a model is often crucial or sometimes even impossible when complex reactions are studied.

MFK does need at least three dynamic curves collected with three different heating rates. The dynamic curves should be calculated to conversion curves. These conversion curves are converted according to the following formula:

$$\ln\frac{\beta}{T_{\alpha}^{2}} = \ln\left(\frac{Rk_0}{E_{\alpha}g(\alpha)}\right) - \frac{E_{\alpha}}{R}\frac{1}{T_{\alpha}} \tag{2}$$

where $\mathrm{d}\alpha/\mathrm{d}t$ – reaction rate/s^{-1}, k_0 – rate constant at an infinite temperature/s^{-1}, α – conversion, β – heating rate/K s^{-1}, E_{α} – activation energy as a function of α/kJ mol^{-1}, R – gas constant/8.314 J mol^{-1} K^{-1} and T_{α} – temperature at a certain α/K.

For every conversion α $\ln(\beta/T_{\alpha}^{2})$ is plotted *vs.* $1/T_{\alpha}$. If this performed for 100 measured conversion values, it results in 100 functions. A straight line with the slope $-(E_{\alpha}/R)$ is the result, and the activation energy is obtained as a function of the conversion.

Modified Kissinger equation

The starting point of many other kinetic calculations is the Arrhenius equation:

$$k_{\mathrm{T}} = A\mathrm{e}^{-\frac{\mathrm{E}}{\mathrm{RT}}} \tag{3}$$

where k_{T} – reaction rate constant, A – frequency factor/min^{-1}, E – activation energy/J mol^{-1}, R – gas constant/8.314 J mol^{-1} K^{-1} and T – temperature/K.

With the modified Kissinger equation [2] the activation energy can be determined, based on TG measurements performed with different heating rates. The Kissinger equation is independent of the order of the reaction. The peak temperatures or the extrapolated onset temperatures of the reaction are used. Because the different measurements are compared to each other, it is important that the sample sizes of the dif-

Table 1 Contents of explosive series 1–3

Series 1	Series 2	Seies 3
Explosive A1992	Explosive H1987	Explosive A1992
Explosive B	Explosive J1989	Explosive H1987
Explosive C1999	Explosive K1990	Explosive M1991
Explosive D1999	Explosive L1993	Explosive N2003
Explosive E1999		Explosive P2003
Explosive F1996		
Explosive G2002		

Table 2 Rough composition of the explosives

	AN	DNT	NG/ EGDN	NH_4Cl	NG	DEGN	InorgMat	NC	TNT	EGDN	Misc.
mass%	%	%	%	%	%	%	%	%			%
Explosive A1992	77	12	4								7
Explosive B				35	6	5					54
Explosive C1999							>70				<30
Explosive D1999*							>70				<30
Explosive E1999*							>70				<30
Explosive H1987	40–50				17–20	17–20		<2	<5		
Explosive J1989	60–70				25–30	0–30					<2
Explosive K1990	50	3				36					11
Explosive L1993	54–61	3.5–6				21–30			3.5–6		
Explosive M1991				34	5					4	57
Explosive N2003				35	6	5					54
Explosive P2003	77	12	4								7

AN=ammoniumnitrate, DNT=dinitrotoluene, NG=nitroglycerine, EGDN=ethyleneglycoldinitrate, NH_4Cl=ammoniumchloride, DEGN=diethyleneglycoldinitrate, InorgMat=inorganic material (inorganic nitrates), NC=nitrocellulose, TNT=trinitrotoluene, Misc.=miscellaneous; *with Al ferent experiments are close together. The used equation is slightly modified as described in [2] and uses the following formula

$$\frac{d\left(\ln\frac{\beta}{T^{2}}\right)}{d\left(\frac{1}{T}\right)}=-\frac{E}{R} \qquad (4)$$

where β – heating rate/K min^{-1}, T – decomposition temperature/K, E – activation energy/J mol^{-1} and R – gas constant/8.314 J mol^{-1} K^{-1}

A graph should be made from $\ln(\beta/T^2)$ *vs.* $1/T$. From the slope of this line the activation energy can be calculated.

The Arrhenius equation (Eq. (3)) is also used for the determination of the storage period equivalent to the artificial aging at (in our study) 50°C.

Sample description

Three different sets of samples are used in this project. All of them are civilian explosives.

The first set contained only unaged samples. The second set of samples was aged for 2, 4 and 6 weeks at 50°C. The unaged samples of this series are also measured. The third set is also aged for 2, 4 and 6 weeks at 50°C. During aging the samples were stored in closed containers. In series 3 every explosive also contains a sample which is aged for 6 weeks in an open container. This sample is called 'open sample'. Table 1 shows the names of the explosives belonging to each set of samples.

From most explosives the composition is roughly known. This is shown in Table 2.

Results

Tables 3–5 the TG results from all delivered samples are shown.

In Table 6 the results of the mass loss during aging of the explosives of series 3 are presented. The result after 4 weeks aging is the mass loss between 2 and 4 weeks aging. The result after 6 weeks aging is the mass loss between 4 and 6 weeks aging. The total aging mass loss is the mass loss during 6 weeks aging.

Figure 1 shows TG curves. The top graph shows the curves of Explosive H1987 series 2, 6 weeks aged. The bottom graph contains the curves of Explosive A1992 series 3, 4 weeks aged. The difference is

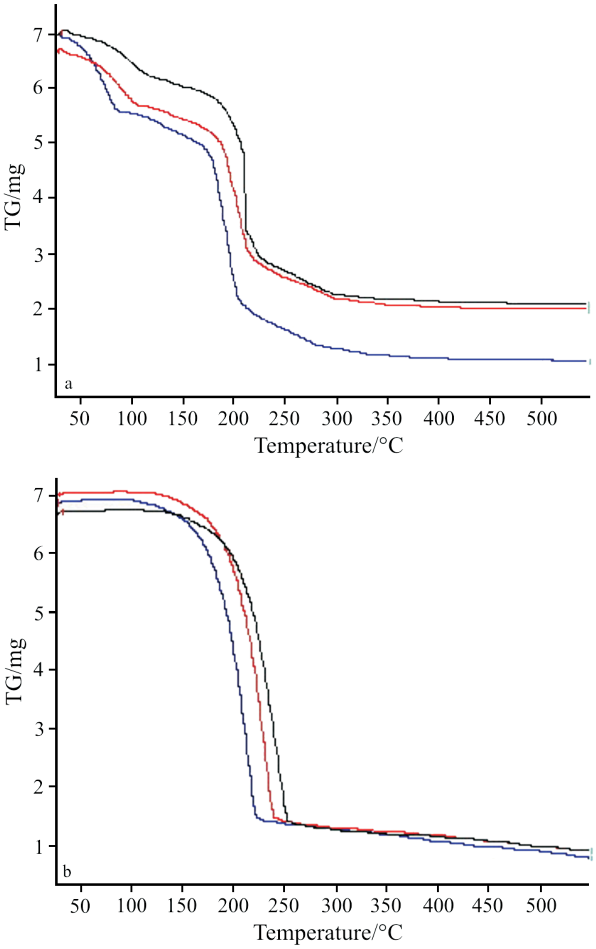

Fig. 1 TG curves of two aged explosives

Table 3 TG results from series 1

β/K min^{-1}		Explosive A1992	Explosive B	Explosive C1999	Explosive D1999	Explosive E1999	Explosive F1996	Explosive G2002
10	T_e/°C	204	202	221	239	235	202	214
	T_{15}/°C	200	212	220	231	229	208	216
	Δm/%	87	50	69	73	78	52	68
5	T_e/°C	193	186	204	215	217	189	208
	T_{15}/°C	189	198	209	217	211	198	204
	Δm/%	86	49	68	71	78	54	69
2	T_e/°C	171	172	187	193	206	178	200
	T_{15}/°C	177	179	187	191	196	184	185
	Δm/%	88	51	69	72	79	48	70

Table 4 TG results from series 2

	β/K min^{-1}		Explosive H1987	Explosive J1989	Explosive K1990	Explosive L1993
Unaged	10	T_e/°C	192	191	194	196
		T_{15}/°C	188	211	212	199
		Δm/%	55	74	52	69
	5	T_e/°C	178	188	184	190
		T_{15}/°C	180	202	201	187
		Δm/%	53	72	56	65
	2	T_e/°C	168	171	177	171
		T_{15}/°C	165	184	185	173
		Δm/%	54	74	56	67
2 weeks aged	10	T_e/°C	–	215	206	208
		T_{15}/°C	–	206	212	200
		Δm/%	–	73	55	69
	5	T_e/°C	–	200	194	202
		T_{15}/°C	–	194	200	189
		Δm/%	–	73	54	71
	2	T_e/°C	–	184	182	187
		T_{15}/°C	–	–	180	170
		Δm/%	–	89	59	71
4 weeks aged	10	T_e/°C	194	210	199	189
		T_{15}/°C	190	211	210	197
		Δm/%	72	73	56	72
	5	T_e/°C	186	202	194	172
		T_{15}/°C	175	202	200	186
		Δm/%	72	75	54	71
	2	T_e/°C	176	180	179	163
		T_{15}/°C	169	182	184	171
		Δm/%	84	78	56	73
6 weeks aged	10	T_e/°C	207	193	204	198
		T_{15}/°C	194	205	210	197
		Δm/%	72	77	57	75
	5	T_e/°C	184	182	191	187
		T_{15}/°C	185	201	199	185
		Δm/%	71	78	54	75
	2	T_e/°C	178	168	181	175
		T_{15}/°C	177	181	182	166
		Δm/%	85	81	48	76

The 2 weeks aged sample from Explosive H1987 was not delivered

clear: the initial mass loss in the first graph is much higher and the pattern is more complex. This is confirmed in Table 6.

Tables 7 and 8 show the results of the kinetic calculations. The activation energy (in kJ mol^{-1}) of the decomposition step is calculated with the different methods. Table 7 contains the results of the unaged samples. Table 8 has the results of the aged samples.

The MFK method results in a function of the activation energy *vs*. conversion. In Tables 7 and 8 the values at a conversion of 50% are given. The calculations with the modified Kissinger equation are performed with the extrapolated onset temperatures (Kis1) and the TG sample temperature at a conversion of 15% of the decomposition step (Kis2).

In Fig. 2 the process of MFK is shown. From the TG curves, conversion curves are calculated. This

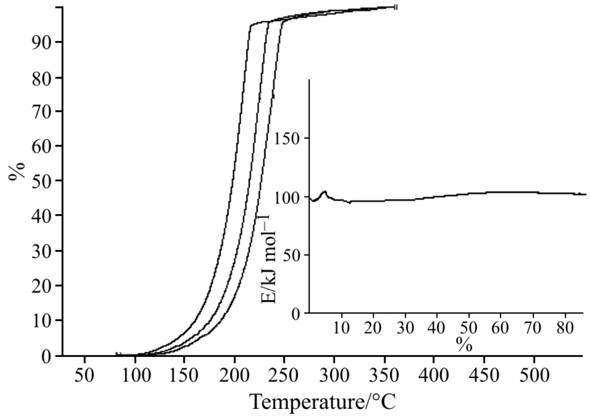

Fig. 2 Model-free kinetics process of Explosive A1992 series 3

Table 5 TG results from series 3

	β/K min^{-1}		Explosive A1992	Explosive H1987	Explosive M1991	Explosive N2003	Explosive P2003
Unaged	10	T_e/°C	201	191	194	195	197
		T_{15}/°C	194	184	190	169	–
		Δm/%	88	54	38	48	59
	5	T_e/°C	186	175	177	183	184
		T_{15}/°C	180	175	176	157	170
		Δm/%	87	55	39	48	58
	2	T_e/°C	172	166	162	166	166
		T_{15}/°C	162	161	160	144	155
		Δm/%	92	53	39	50	58
2 weeks aged	10	T_e/°C	193	186	197	194	198
		T_{15}/°C	195	185	187	173	183
		Δm/%	87	54	40	48	57
	5	T_e/°C	181	177	179	184	183
		T_{15}/°C	180	176	174	159	170
		Δm/%	87	54	38	49	57
	2	T_e/°C	175	167	164	164	171
		T_{15}/°C	169	161	–	146	154
		Δm/%	90	53	41	49	57
4 weeks aged	10	T_e/°C	200	189	197	195	195
		T_{15}/°C	194	185	189	178	177
		Δm/%	87	55	40	48	56
	5	T_e/°C	184	175	181	179	184
		T_{15}/°C	183	174	177	163	172
		Δm/%	88	55	39	47	57
	2	T_e/°C	173	167	166	166	169
		T_{15}/°C	166	165	161	–	155
		Δm/%	89	57	39	50	59
6 weeks aged	10	T_e/°C	206	185	196	192	195
		T_{15}/°C	197	184	188	174	184
		Δm/%	88	54	39	49	57
	5	T_e/°C	189	178	185	181	184
		T_{15}/°C	184	176	175	165	172
		Δm/%	88	54	41	48	57
	2	T_e/°C	174	165	165	161	172
		T_{15}/°C	171	160	160	150	157
		Δm/%	90	52	41	49	57
open sample, 6 weeks aged	10	T_e/°C	206	183	197	190	193
		T_{15}/°C	201	185	188	190	196
		Δm/%	91	76	42	49	57
	5	T_e/°C	194	176	187	179	186
		T_{15}/°C	188	173	174	178	182
		Δm/%	92	75	43	49	57
	2	T_e/°C	178	169	171	166	169
		T_{15}/°C	173	163	158	161	165
		Δm/%	92	73	45	50	59

β – heating rate, T_e – extrapolated onset temperature of the decomposition step, T_{15} – sample temperature at a conversion of 15% of the decomposition step and Δm – total mass loss

three conversion curves result in a graph of the activation energy *vs*. conversion.

The difference in results found for the several explosives is due to the fact that

- some explosives contain volatiles, which disappear during the TG measurements
- extrapolated onset temperatures are much more subjective to determine compared to the 15% conversion temperature
- the beginning and end of the decomposition step is not clear in some TG curves

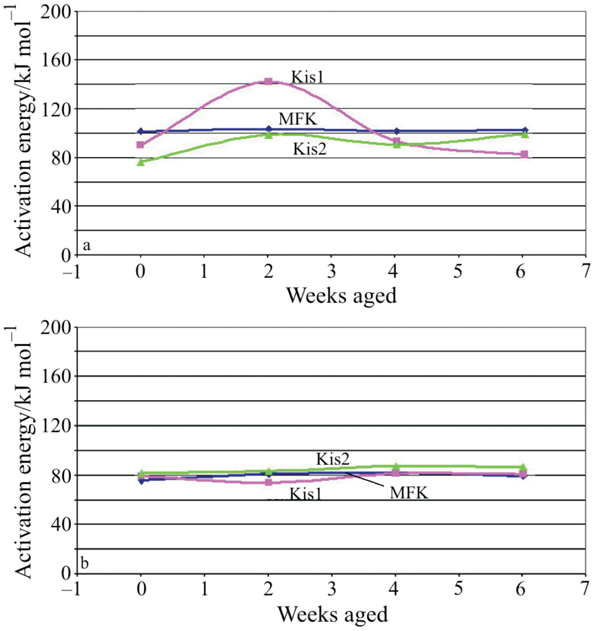

Fig. 3 Activation energy calculated *vs*. the aging period; a – Explosive A1992 serie 3, b – Explosive M1991

Table 7 Activation energy (kJ mol^{-1}) of the unaged samples

	MFK	Kis1	Kis2
Explosive A1992 series 1	112	76	115
Explosive A1992 series 3	101	90	76
Explosive B	84	86	79
Explosive C1999	93	82	82
Explosive D1999	77	61	70
Explosive E1999	91	101	87
Explosive F1996	119	153	112
Explosive G2002	146	212	88
Explosive H1987 series 2	102	105	109
Explosive H1987 series 3	106	98	106
Explosive J1989	91	114	96
Explosive K1990	100	107	104
Explosive L1993	99	94	98
Explosive M1991	76	79	82
Explosive N2003	84	85	90
Explosive P2003	89	82	91

In Fig. 3, the dependence of the activation energies found to the aging period is shown.

Discussion

TG results

All TG curves show a decomposition step, together with a large mass loss between 160°C (at 2 K min^{-1}) and roughly 190°C (at 10 K min^{-1}).

Some explosives have a mass loss before the decomposition, due to the loss of some solvents or other volatile components. It is not clear from the rough composition of the explosives what component is exactly lost. It could be moisture, because of the fact that in most cases the mass loss stops around 100°C, but e.g. in Explosive H1987 serie 3 also after 100°C mass loss occurs which is not due to the decomposition which starts later during the process. FTIR or MS spectrometry can be used to determine the nature of the volatiles. These techniques are available at TNO–PML but are currently not used in this study.

Aging of the explosives does not have a dramatic effect on the resulting onset temperatures. The onset temperatures show some deviation but that is more due to the method used (sample size, heating rate, flow rate, etc.) than as a result of aging.

The total mass loss differs from explosive to explosive. They all have a different composition. Explosives A1992 and H1987 are measured twice and the results are in good correlation with each other.

Mass loss during aging

The results shown in Table 6 give the same trend in mass loss for all explosives. The open samples have a

Table 6 Mass loss during aging

	Sample container	2 weeks aging	4 weeks aging	6 weeks aging	Total aging mass loss
		mass loss/%			
Explosive A1992 series 3	closed	0.89	0.79	0.79	2.45
	open	5.39	0.25	0.20	5.81
Explosive H1987 series 3	closed	0.77	0.69	0.66	2.09
	open	14.75	10.12	8.68	30.03
Explosive M1991	closed	3.64	1.10	0.48	5.15
	open	6.64	0.31	0.38	7.76
Explosive N2003	closed	1.30	0.69	0.82	2.78
	open	5.86	1.45	1.31	8.44
Explosive P2003	closed	0.60	0.40	0.44	1.51
	open	5.90	1.11	0.76	7.66

Table 8 Activation energy (kJ mol^{-1}) of the aged samples

	2 weeks aged			4 weeks aged			6 weeks aged			Open sample		
	MFK	Kis1	Kis2	MFK	Kis1	Kis2	MFK	Kis1	Kis2	MFK	Kis1	Kis2
Explosive H1987 series 2	–	–	–	96	147	115	105	79	159	–	–	–
Explosive H1987 series 3	110	135	103	116	112	124	90	125	101	112	189	111
Explosive J1989	96	86	60	91	85	88	105	103	102	–	–	–
Explosive K1990	105	109	92	103	130	104	102	116	98	–	–	–
Explosive L1993	114	129	95	107	93	102	109	114	81	–	–	–
Explosive A1992 series 3	103	142	99	102	93	91	102	82	99	101	94	93
Explosive M1991	81	74	83	82	81	87	80	81	86	84	96	84
Explosive N2003	83	80	87	81	88	70	86	78	95	81	104	84
Explosive P2003	83	97	82	91	100	102	88	110	88	84	105	81

higher mass loss than the closed ones, which confirms the suggestion that the unaged samples contain some volatiles. Explosive H1987 shows the highest mass loss, which is also confirmed in the TG curves. There is a significant mass loss before the real start of the decomposition.

Activation energy

From Tables 6 and 7 and Fig. 3 it can be concluded, that the used kinetic models, almost give the same results. Looking more in detail to the results, it appears that the results from MFK and Kis2 are almost the same. The results for Kis1 have more deviation, because of the difficulty to determine the onset temperature in an objective way.

The aging of the explosives does not have any influence on the activation energy. Six weeks of artificial aging at 50°C corresponds to a storage period at 20°C for 5 years, when using average activation energy of 100 kJ mol^{-1}. This means that the examined explosives are thermally stable for at least 5 years considering storage at 20°C. This is also confirmed by the values of the onset temperatures. Storage at a lower temperature results in even longer storage time.

Conclusions

TG is a quick and reliable method to determine the lifetime of commercial explosives.

Some explosives contain volatiles which disappear before the decomposition starts.

MFK and the modified Kissinger equation give the same results for the activation energy calculated.

All measured explosives show no change in activation energy due to aging, which means that they are thermally stable for at least 5 years, which is also confirmed by the found onset temperatures.

Abbreviations

AN	ammoniumnitrate
DEGN	diethyleneglycoldinitrate
DNT	dinitrotoluene
EGDN	ethyleneglycoldinitrate
InorgMat	inorganic material (inorganic nitrates)
MFK	model-free kinetics
Misc.	miscellaneous
NC	nitrocellulose
NG	nitroglycerine
NH_4Cl	ammoniumchlorate
PML	Prins Maurits Laboratory
SDTA	single differential thermal analysis
TG	thermogravimetry, thermogravimetric analysis
TNO	Toegepast Natuurwetenschappelijk Onderzoek (applied scientific research)
TNT	trinitrotoluene

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