Journal of Thermal Analysis and Calorimetry, Vol. 85 (2006) 1, 203–207

AGEING STUDIES OF MAGNESIUM–SODIUM NITRATE PYROTECHNIC COMPOSITIONS

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The ageing characteristics of pyrotechnic compositions are influenced not only by temperature, but also by surrounding effects as humidity and vibrations. In this paper the thermal stability of the pyrotechnic system magnesium–sodium nitrate will be investigated.

In an inert helium atmosphere two steps of mass loss, which were not completely separated from each other, were observed in the temperature range from 65 to 265°C: a mass loss of about 15% between 65 and 160°C and about 34% between 160 and 265°C. It is assumed that these two steps are caused by different processes. The separation between the two steps was not or hardly detectable for measurements that were performed in a nitrogen atmosphere. Using MS and FTIR (mass spectrometry/Fourier transform infrared spectroscopy) the evolved gases were analysed. Only above about 170°C evolving gases were detected (which means that during the first step no gases were detectable). The detected gas mainly consists of CO_2, CO and N_2O, with smaller amounts of NO_2, NO and possibly HCN. A third step of mass loss (8–9%) was observed above 314°C. The process which caused this step of mass loss is considered not to contribute significantly to the ageing of the material at much lower temperatures of maximum 80°C, which is of interest in view of the use of the materials.

Kinetic parameters for the processes which caused the first and the second step of mass loss were evaluated from kinetic analysis of the measured TG curves. By using these results the conversion can be predicted as a function of time and temperature. However, it must be considered that the inaccuracy of the predictions increases if the temperature for which the prediction is calculated is further away from the temperature at which the experiments were performed. This is caused by the exponential form of the kinetic equations. The calculations show that in particular the reaction which causes the first step of mass loss can run relatively quickly in the temperature range 25–80°C, which could result in ageing of the material during storage at these conditions. The reaction which causes the second step of mass loss clearly runs at a much lower rate.

Keywords: *kinetic analysis, lifetime studies, magnesium, thermal analysis, tracer*

Introduction

The majority of munitions spend most of their service life in storage. The period spent in operational use will be shorter and packaging (if used) may be much lighter. Adequate protection is required during all these periods. So suitable packaging of munitions is essential to maintain safety, serviceability and reliability by protecting the munition against extremes of temperature, humidity, vibration, shock and other environmental hazards. The packaging should be constructed of compatible materials which do not affect or contaminate the munition.

During the last five years it has became of more importance to investigate the stability, or more realistic, the functional lifetime of different pyrotechnic systems, which are in use by the National Forces. One of the frequently used materials will be the decay compositions for different purposes. For these materials it is of great importance that they will function correctly and within the right time.

For this study a composition of magnesium, sodium nitrate and additives is primarily investigated by thermal techniques like TG, DSC and mechanical analysis in combination with chemical analysis.

The investigated pyrotechnic composition contains magnesium as fuel and sodium nitrate as oxidizer (identified by X-ray diffraction and scanning electron microscopy) in an organic binder. The basic elements of the binder are carbon, nitrogen and oxygen. The first range of samples which were investigated by TG/DTA, consisted of pieces of 2–3 mg of the material, collected after cutting the cube-form material with a knife, without any further pre-treatment. However, the obtained experimental results reproduced very badly. This is caused by the inhomogenity of the material in combination with the small sample masses. This may have resulted in a variation of the chemical composition of the investigated samples. This problem can be partly solved by crushing the material, which, however, appeared to be difficult. As an alternative, mixing very small particles that were cut from a significant part of the material appeared to be successful: good reproducibility was obtained using samples of 2 to 3 mg.

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1388–6150/$20.00

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Experimental

TG measurements were performed on a Mettler Toledo TGA/SDTA 851^e. Standard Aluminum sample vessels were used (volume 40 μL). These sample cups were closed with a pierced lid with a hole of ~1 mm. The diameter in relation to the volume of the sample vessel was large enough to avoid the diffusion problems. During the measurements helium or nitrogen was used as carrier gas (75 mL min^{-1}). In a few experiments the TG was simultaneously coupled with FTIR/MS to identify the decomposition gases. For kinetic analysis experiments were performed using different heating rates between 1 and 5 K min^{-1}.

The material for this study was from a pyrotechnic system which was stored under ambient storage conditions, which are controlled by temperature and humidity.

Kinetic study

With thermal techniques like DSC and TG/DTA it is feasible to perform kinetic calculations based on the conversion degree (α). During the measurements the changes are measured as a function of time, while the investigated sample follows a temperature program. This results in the scientific way to use thermal analysis for kinetic investigations. Most of the time the experiments are carried out with a linear heating rate, β. The rate Eq. (1) can easily be transformed from a time-dependency to a temperature dependency (2)

$$d\alpha/dt=k_0\exp(-E_a/RT)f(\alpha) \qquad (1)$$

where $d\alpha/dt$=reaction rate/s^{-1}, k_0=rate constant at an infinite temperature/s^{-1}, α=conversion, E_α=activation energy as a function of α/kJ mol^{-1}, R=gas constant/8.314 J mol^{-1} K^{-1}.

$$d\alpha/dT=(d\alpha/dt)(dt/dT)=\frac{d\alpha/dt}{dT/dt} \qquad (2)$$

Because of the fact that the part (dT/dt) is equivalent to the linear heating rate, β, Eq. (1) can be rewritten by substitution of Eq. (2) to:

$$d\alpha/dT=(d\alpha/dt)/\beta=(k_0/\beta)\exp(-E_a/RT)f(\alpha) \qquad (3)$$

where β=heating rate/K s^{-1}.

This can also be written as:

$$\ln\{\beta(d\alpha/dT)\}=-E_a/RT+\ln\{k_0f(\alpha)\} \qquad (4)$$

A well-known problem is the fact that in most situations, the function $f(\alpha)$ is unknown, or very difficult to determine. In the methodology of 'model-free kinetics' (MFK) [1, 2], this function is eliminated. 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:

$$\ln\frac{\beta}{T_\alpha^2}=\ln\left[\frac{Rk_0}{E_\alpha g(\alpha)}\right]-\frac{E_\alpha}{R}\frac{1}{T_\alpha} \qquad (5)$$

where 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 is 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.

Results and discussion

TG curves, recorded during measurements performed in a helium atmosphere, show two decomposition steps (mass loss) in the temperature range between 65 and 275°C (Fig. 1). These steps were not completely separated from each other. The mass loss was about 15% between about 65 and 160°C and about 34% between about 160 and 265°C. A third decomposition step (mass loss 8–9%) was observed above 314°C; because of the high temperature at which this step occurs, it is assumed to have no influence on ageing during storage at regular temperatures.

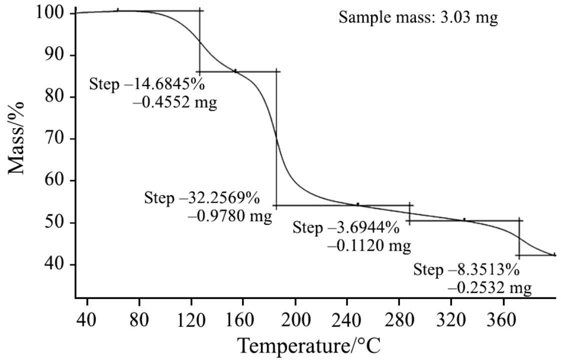

Fig. 1 TG curve on the magnesium–sodium nitrate mixture at 5 K min^{-1}, He atmosphere

Only during the second mass loss step, above 170°C, a detectable amount of decomposition gases was observed. The composition of the gas was identified by FTIR/MS as mainly CO_2, CO, N_2O and smaller amounts of NO_2, NO and possibly some HCN. The HCN could be a decomposition product of the organic binder.

In a nitrogen atmosphere the first step shifts to a higher temperature, which causes a higher degree of overlapping with the second step. It is a well-known fact that reactions in which gaseous reactants or products are involved are influenced by the partial pressures of these gases. It is surprising that differences were observed for the measurements in helium and nitrogen, because both gases are considered to be inert. An explanation could be the influence of nitrogen on the NO_x equilibrium.

The kinetic analyses were more complicated because of the fact that the processes which occur are not completely clear. Because of this uncertainty it is assumed that two different decomposition processes occur below temperatures of 275°C, which are kinetically analyzed separately. The kinetic analyses were performed on the TG experiments which were carried out under a helium atmosphere using several heating rates between 1 and 5 K min^{-1}. The MFK philosophy was used for the calculations of the activation energy as a function of the conversion from conversion–temperature curves that were evaluated from the experimental TG curves (Figs 2 and 5 for the first and the second reaction step, respectively). The evaluated kinetic parameters were used for the calculations of the conversion as a function of time at several temperatures, as presented in Figs 3 and 6 for the first and the second reaction step, respectively. Finally some

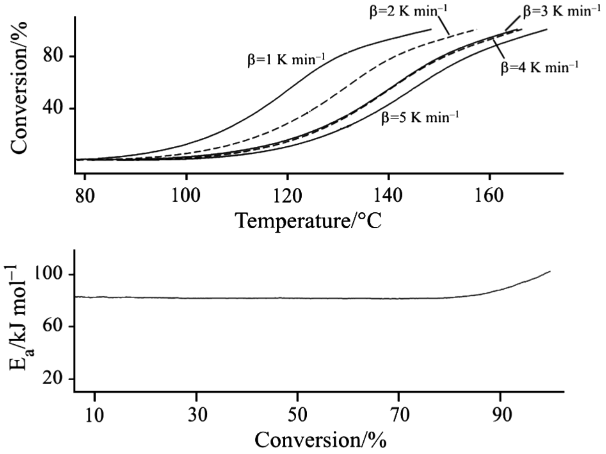

Fig. 2 Conversion *vs.* temperature curves obtained from the experimental TG curves together with the evaluated activation energy as a function of conversion for the first step of the reaction

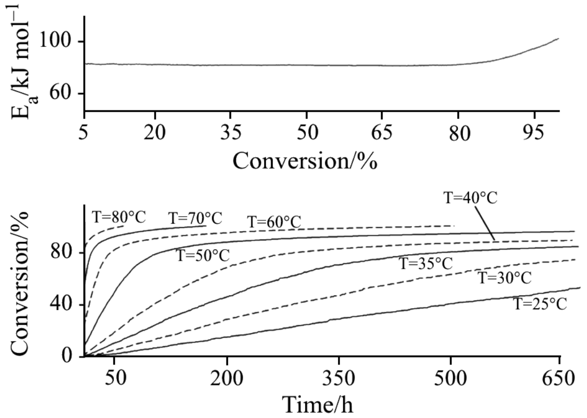

Fig. 3 Calculated conversion as function of time at several temperatures for the first step of the reaction

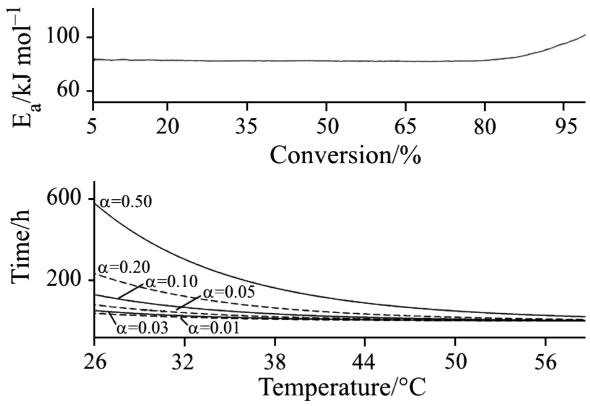

Fig. 4 Calculated isoconversion curves for the first step of the reaction

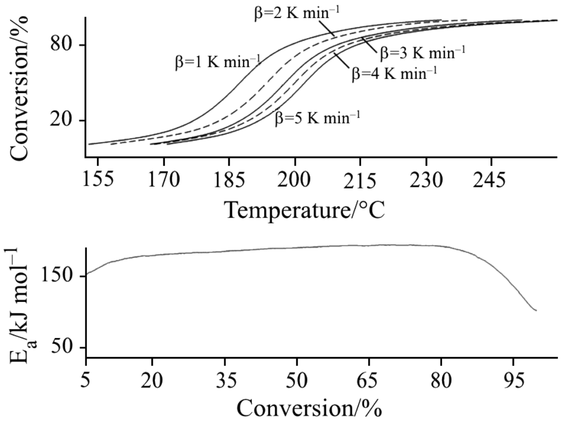

Fig. 5 Conversion *vs.* temperature curves obtained from the experimental TG curves together with the evaluated activation energy as a function of conversion for the second step of the reaction

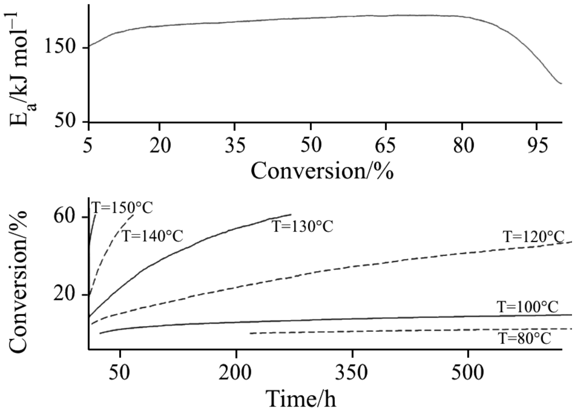

Fig. 6 Calculated conversion as function of time at several temperatures for the second step of the reaction

Table 1 Time after which the first reaction is expected to reach a certain amount of conversion at a specific temperature

α	Time/h					
	25°C	40°C	50°C	60°C	70°C	80°C
0.01	38	8	2.8	1.1	0.5	0.2
0.02	56	11	4.1	1.6	0.7	0.3
0.03	68	14	5.1	2.0	0.8	0.4
0.05	89	18	6.9	2.7	1.1	0.5
0.07	114	23	8.7	3.5	1.5	0.6
0.10	147	30	11	4.5	1.9	0.8
0.15	205	42	16	6.3	2.7	1.2
0.20	263	54	20	8.1	3.4	1.5
0.25	316	65	25	9.9	4.2	1.9
0.30	366	78	29	12	5.0	2.2
0.50	645	134	51	20	8.7	3.4

Table 2 Time after which the second reaction is expected to reach a certain amount of conversion at a specific temperature

α	Time/h					
	80°C	100°C	120°C	130°C	140°C	150°C
0.01	337	33	4.1	1.6	0.64	0.27
0.02	512	48	5.5	2.0	0.79	0.32
0.03	–	70	7.5	2.7	0.99	0.39
0.05	–	147	13	4.5	1.6	0.57
0.07	–	298	24	7.3	2.4	0.82
0.10	–	–	48	14	4.1	1.3
0.15	–	–	99	26	7.5	2.2
0.20	–	–	153	40	11	3.2
0.25	–	–	217	55	15	4.3
0.30	–	–	283	71	19	5.4
0.50	–	–	–	171	44	12

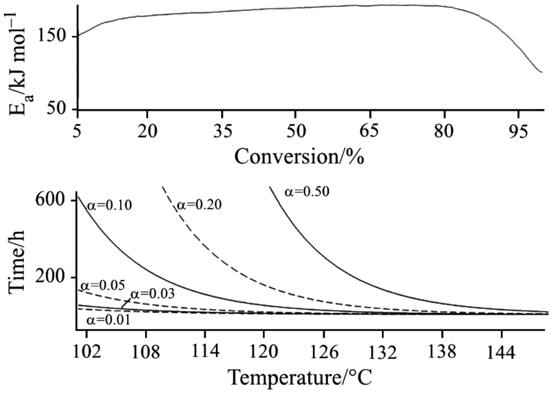

Fig. 7 Calculated isoconversion curves for the second step of the reaction

isoconversion curves were calculated for the two reactions (Figs 4 and 7). For the first and the second reaction steps in Tables 1 and 2, respectively, the estimated times are presented at which a certain degree of conversion is reached for specified temperatures.

Conclusions

The TG experiments show that under an inert gas in the temperature range from 65 to 265°C, two thermal effects occur that are associated with mass loss (indication of decomposition). The two steps are not completely separated, and correspond with a mass loss of ~15 and ~34%. The decomposition gases were analyzed by MS and FTIR. Up to about 170°C (temperature range of the first mass loss step) no significant signals which correspond to gases from the sample material were observed. Above 170°C (temperature range of the second mass loss step) the gas from the sample material was found to contain mainly CO_2, CO and N_2O, with probably small traces of NO_2, NO and possibly some HCN.

The third step, with a mass change of (8 to 9%) is recorded above a temperature of 314°C. For this process the assumption is made that it will have a negligible influence on the decomposition process at temperatures below 80°C.

The first two steps are separately analyzed using the MFK method, with the assumption that the two processes are independent of each other. The results of the kinetic analyses make it feasible to calculate the conversion degree as function of time and temperature. At realistic storage conditions, even in hot areas, the temperature will not exceed 70°C. For the investigated material especially the first decomposition step may be of influence at these conditions: e.g. at 70°C a conversion of 1% is expected after about half an hour (Table 1 and Fig. 3)! The influence of the second decomposition step is expected to be much smaller: only 2% conversion after ~20 days at 80°C (Table 2 and Fig. 6). Of course there is an error in extrapolating the values of higher temperatures to lower temperatures, because of the exponential curves, but the calculated values will give a good indication of the magnitude of conversion.

To find out whether the observed processes really have an influence on the functionality of the article after storage under these conditions further investigations are required because e.g. the packaging of the product can have a significant influence.

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DOI: 10.1007/s10973-005-7422-0