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NON-ISOTHERMAL KINETIC STUDY OF THE THERMAL DECOMPOSITION OF DIAMINOGLYOXIME AND DIAMINOFURAZAN

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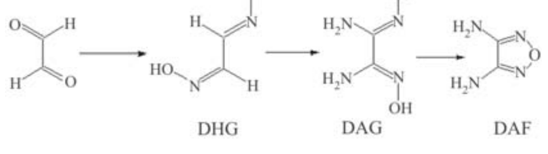
Data on the thermal stability of organic materials such as diaminofurazan (DAF) and diaminoglyoxime (DAG) was required in order to obtain safety information for handling, storage and use. These compounds have been shown to be a useful intermediate for the preparation of energetic compounds. In the present study, the thermal stability of the DAF and DAG was determined by differential scanning calorimetery (DSC) and simultaneous thermogravimetery-differential thermal analysis (TG-DTA) techniques. The results of TG analysis revealed that the main thermal degradation for the DAF and DAG occurs in the temperature ranges of 230–275°C and 180–230°C, respectively. On the other hand, the TG-DTA analysis of compounds indicates that DAF melts (at about 182°C) before it decomposes. However, the thermal decomposition of the DAG started simultaneously with its melting. The influence of the heating rate (5, 10, 15 and 20°C min^{-1}) on the DSC behaviour of the compounds was verified. The results showed that, as the heating rate was increased, decomposition temperatures of the compounds were increased. Also, the kinetic parameters such as activation energy and frequency factor for the compounds were obtained from the DSC data by non-isothermal methods proposed by ASTM E698 and Ozawa. Based on the values of activation energy obtained by ASTM and Ozawa methods, the following order in the thermal stability was noticed: DAF>DAG.

Keywords: *activation energy, diaminofurazan, diaminoglyoxime, DSC, non-isothermal, Ozawa, TG/DTA*

Introduction

During the course of recent studies directed toward the synthesis of new energetic materials, the furazan ring has been found to be a useful substructure for the design of new high density, high energy materials composed exclusively of carbon, hydrogen, nitrogen and oxygen atoms [1, 2]. Diaminofurazan (3,4-diamino-1,2,5-oxadiazole) has been shown to be a useful intermediate for the preparation of energetic compounds [3–6]. In addition, it has been identified as a urea equivalent for histamine H_2-receptor antagonists [7–9]. Moreover, diaminofurazan has recently been employed as a subunit for the construction of crown ethers and macrocycles [10, 11]. On the other hand, as illustrated in Scheme 1, diaminofurazan could be generated from the dehydration of diaminoglyoxime. Therefore, the preparation of DAF has been limited by the availability of the precursor diaminoglyoxime (DAG) [12–15].



Scheme 1 The synthesis of DAG and DAF achieved in two and three steps from commercially available glyoxanal [13, 14]

Compatibility studies of different materials by DSC, DTA and TG have been carried out for several years [16–20]. Kinetic studies have become a crucial point in thermal analysis, in which the main purpose is to determine the mechanism of pyrolysis reaction and to calculate the parameters of the Arrhenius equation. These data are required for energetic materials and their related compounds to be qualified for performance and safety in their manufacture, handling, storage and use [21, 22].

In this work, the DAF and DAG compounds were investigated by means of DSC and TG-DTA. The results allowed us to acquire information concerning these compounds in the solid-state, including their thermal stability and thermal decomposition. Also, this study seeks for determination of kinetic parameters of non-isothermal decomposition of the compounds. To the best our knowledge, the thermolysis of DAG and its application in double base propellant have been reported [23], previously. But there is no report on the thermal behaviour of DAF.

Experimental

The diaminoglyoxime and diaminofurazan compounds were synthesized as proposed by [13]. The DSC curves were obtained by DuPont differential scanning calo-

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rimeter model DSC 910S, in temperature range of 50–500°C using an aluminum crucible, at different heating rates (5, 10, 15 and 20°C min^{-1}), under nitrogen atmosphere with the flow rate of 50 mL min^{-1}.

TG and DTA were carried out using a Stanton Redcroft, STA-780 series with an alumina crucible, applying heating rate of 10°C min^{-1} in a temperature range of 50–500°C, under nitrogen atmosphere with the flow rate of 50 mL min^{-1}. The sample mass used was about 3.0 mg.

Results and discussion

The thermoanalytical curves of DAF are presented in Fig. 1a. The DTA curve showed a broad endothermic behaviour commencing near 182°C, which is the melting point of DAF. Up to the melting point the DAF is thermally stable. However, at higher temperatures, DAF presents a significant mass loss step between 230 and 275°C, which in this step, Δm_1=74% and T_{peak} DTA=245°C. Over 275°C, the TG curve indicates a slow and continuous mass loss caused by elementary carbon formation from the previous step.

The simultaneous TG-DTA curves of the DAG are shown in Fig. 1b. The mass loss (Δm=81%) occurs in the range 180–245°C. After this, a slow and continuous mass loss was observed until 490°C. According to the DTA data, an endothermic peak was observed about 192.5°C corresponding to the melting point of DAG. Also, it was verified that the mass loss for the DAG started simultaneously at its melting point.

Effect of heating rate

Figure 2 shows DSC curves of the decomposition of DAF and DAG at several heating rates. It was found that, by increasing the heating rate, the melting peaks and the decomposition temperature of the DAF and DAG was shifted to higher temperatures. For DAG, the endothermic peak due to DAG melting followed by the exothermic decomposition. By increasing heating rates, the distance between melting peak and decomposition was decreased and at 20°C min^{-1}, de-

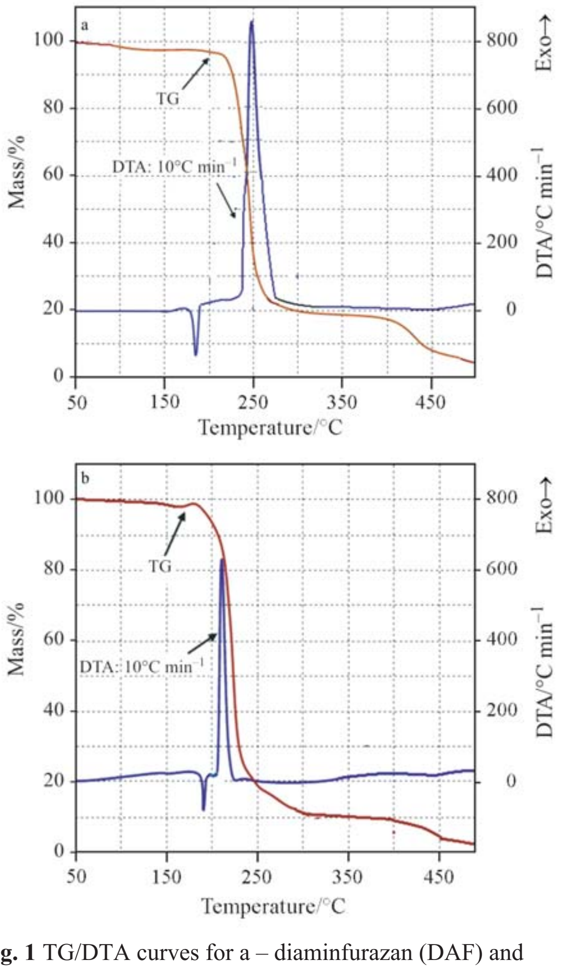

Fig. 1 TG/DTA curves for a – diaminfurazan (DAF) and b – diaminoglyoxime (DAG); sample mass 3.0 mg; heating rate 10°C min^{-1}

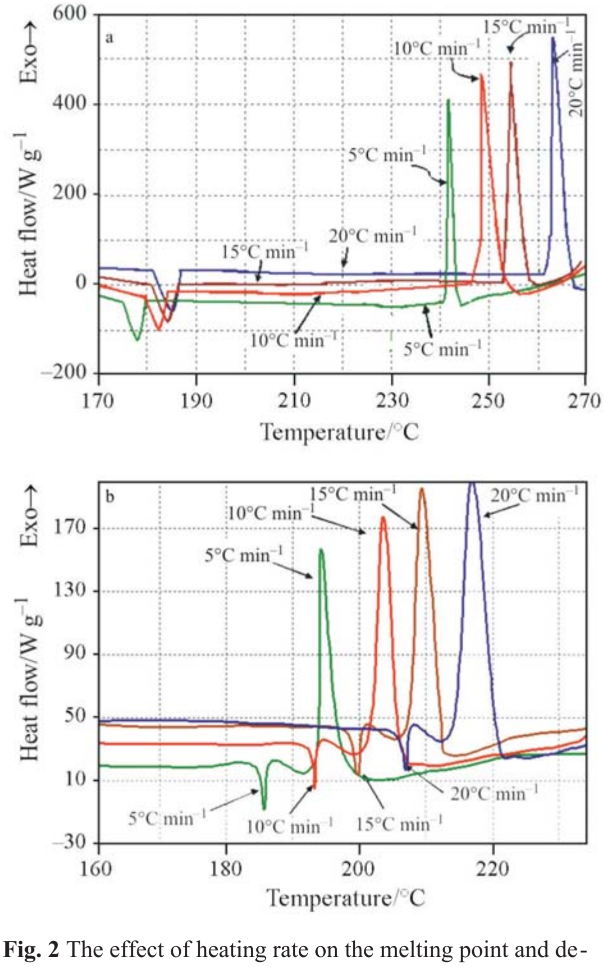

Fig. 2 The effect of heating rate on the melting point and decomposition temperature of a – diaminfurazan (DAF) and b – diaminoglyoxime (DAG); sample mass 3.0 mg

composition was started immediately after melting. On the other hand, at higher heating rates the decomposition of DAF begins in about 260°C and there is a shoulder after the peak. At lower heating rate (5°C) there is a change in the shape of the curve and the shoulder after the decomposition peak disappeared.

Kinetic methods

The ASTM method E698 [24] was used to determine the Arrhenius parameters for the thermal decomposition of DAF and DAG. In order to calculate the pre-exponential factor (Z), it was assumed that the decomposition followed first-order kinetics. The DSC curves obtained at various heating rates for DAF and DAG are shown in Fig. 2. Also, Table 1 summarizes the experimental results as well as the maximum peak temperatures (T_m) for each compound and heating rates (β) used to perform the calculations in the ASTM E698 method.

The plot of the $\ln(\beta T_m^{2-})$ *vs.* $1/T_m$ was straight lines for DAF (r=0.9910) and DAG (r=0.9955), which indicated that the mechanism of thermal decomposition of these compounds is the first order [25]. The slope of the lines was equal to $-E_a/R$. Therefore, the activation energy (E_a) was obtained from the slope of the graph while the log of the pre-exponential factor, $\log(Z/S^{-1})$ was calculated from the expression given in ASTM E698: $Z=\beta(E_a/RT_m^2)\exp(E_a/RT_m)$. Table 2 contains the calculated values of activation energy and frequency factors for both compounds.

On the other and, activation energy (E_a) for these compounds was calculated by Ozawa method. In this method, activation energy could be determined from plots of the logarithm of the heating rate *vs.* the inverse of the temperature at the maximum reaction rate in constant heating rate experiments. The activation energy can be determined by this method without a precise knowledge of the reaction mechanism, using the following equation:

$$\log\beta+0.456E_a/RT_m=C$$

The plot of logarithm of heating rates *vs.* reciprocal of the absolute peak temperature for DAF and DAG was straight lines with r=0.9912 and 0.9962, respectively, which indicated that the mechanism of thermal decomposition of these compounds over this temperature range did not vary [26]. On the other hand, frequency factor (Z) was found for both compounds from the following relation [24, 25]:

$$Z=\beta E\exp(E/RT_m)]/RT_m^2$$

All resulted data are summarized in Table 2. Comparing the results of the application of the two methods, we observe that values calculated for both compounds by ASTM method are slightly higher than those of Ozawa methods. However, both methods reveal the same trend of activation energies for the whole conversion range studies.

Half-life determination

Assuming a first-order decomposition, the equation to determine the half-life is: $t_{1/2}=0.693/k$. The rate constant (k) for decomposition reaction could be calculated by the following equation [26]:

$$\log k = \log Z - E_a/2.3RT$$

which for the temperature of 50°C and using activation energies (E_a) and frequency factors (Z) obtained in the above; the equation was solved for k. Then half-lives of the compounds were predicted. Table 2 listed the half-life for each compound. By considering

Table 1 Melting point and decomposition temperature of diaminofurazan (DAF) and diaminoglyoxime (DAG) obtained by DSC at various heating rate

Compound	DAF		DAG	
Heating rate/°C min^{-1}	melting point/°C	decomp. temp./°C	melting point/°C	decomp. temp./°C
5	178.8	242.8	183.3	195.3
10	181.8	249.6	192.5	204.9
15	182.7	255.1	199.6	212.4
20	183.8	262.5	206.9	218.6

Table 2 Comparison of kinetic parameters of the DAF and DAG obtained by ASTM and Ozawa methods

Compound	ASTM method			Ozawa method		
	E_a/ kJ mol^{-1}	frequency factor $\log Z$/s^{-1}	half-life/ year	E_a/ kJ mol^{-1}	frequency factor $\log Z$/s^{-1}	half-life/ year
DAF	154.8	15.26	135.5	156.5	15.44	171.0
DAG	106.3	11.34	0.016	108.7	11.61	0.021

half-life calculated for DAF using kinetic parameters obtained by different methods, DAF half-life was compared with DAG half-life. It was found that the half-life of DAF is much higher than that calculated for the DAG.

Conclusions

The thermal stability of diaminofurazan (DAF) and diaminoglyoxime (DAG) was determined by differential scanning calorimetery (DSC) and simultaneous differential thermal analysis and thermogravimetry (TG/DTA). Also, the influence of the different heating rates on the DSC behaviour of the compounds was verified. Activation energies and frequency factors for the decomposition were calculated by different methods.

According to the TG/DTA data it was verified that the thermal decomposition of DAG started simultaneously at its melting point. However, DAF was decomposed at about 230°C, after its melting at temperature of 182°C. Based on the kinetic data obtained for the activation energy by ASTM and Ozawa methods, using non-isothermal thermogravimetry experiments, the following stability order for the compounds was established: DAF>DAG.

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