Thermochimica Acta 632 (2016) 46–51

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Isoconversional approach for the non-isothermal decomposition kinetics of guanylurea dinitramide (GUDN)

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ARTICLE INFO

Article history:
Received 29 December 2015
Received in revised form 9 March 2016
Accepted 11 March 2016
Available online 15 March 2016

Keywords:
Isoconversional methods
Kinetics
Guanylurea dinitramide
TGA
Activation energy
Kissinger method

ABSTRACT

The thermal decomposition of a high-energy oxidizer viz., guanylurea dinitramide (GUDN) has been studied by non-isothermal thermogravimetry (TG) and thermogravimetry combined with mass spectrometry (TG-MS). Isoconversional method of Vyazovkin (VZ) was used to investigate the dependence of activation energy (E_a) on conversion (α). A strong dependence of E_a on α, where the E_a increases steadily for up to an α of ~0.6 followed by a marginal increase and reaches ~435.0 kJ mol^{-1} at the end of the reaction. E_a has also been determined for GUDN using Kissinger's method. A comparison of the results from Kissinger and isoconversional method shows that the activation energies from these methods are comparable. Using the model free isoconversional method, the isothermal conversion as a function of time at two different temperatures was also computed. The evolved gases during the decomposition of GUDN were analyzed by TG-MS which revealed the formation of ions corresponding to N_2, O_2, NH_3, H_2O, N_2, NO, methane diimine, isocyanic acid, N_2O, NO_2 and urea.

1. Introduction

Energetic materials find extensive use in composite propellants and explosives. Dinitramide salts occupy the class of new-high energy oxidizers and many of these were synthesized and characterized for military and space applications [1]. Among the dinitramide salts reported, the important ones that have attracted extensive interest are ammonium dinitramide (ADN), potassium dinitramide (KDN) and guanylurea dinitramide (GUDN). ADN is emerging as a promising candidate for replacing the conventional ammonium perchlorate (AP) used in composite solid propellants [2], while GUDN or FOX-12 is a nitrogen rich dinitramide salt (structure shown in Fig. 1) which is intended for use as low-sensitivity oxidizer for propellants and explosives [3]. Its excellent thermal stability along with very low mechanical sensitivity, non hygroscopicity and fairly higher bulk density finds potential use as insensitive munitions and as gas generators [3–8]. Its synthesis [9–11], thermal decomposition kinetics [9,12–14], dissolution properties [15,16] toxicological aspects and photo degradation studies [17,18] have been reported. Limited studies have been carried on the thermal decomposition of GUDN and kinetics were derived using model fitting methods [9,12–14]. Ostmark et al., have studied the thermal stability of GUDN by DSC and the sensitivity to thermal ignition was measured using Wood's metal bath technique and the kinetic parameters were derived using ASTM E 698–79 [9]. Santhosh et al., have studied the decomposition of GUDN by DSC and the activation energy was calculated by Kissinger method [12]. Zhao et al., have studied the thermal decomposition of GUDN by DSC and the kinetic parameters were derived using both Kissinger and Ozawa methods [13]. The kinetic behaviour and decomposition of GUDN was studied by Gao et al., using a DSC and microcalorimeter and the decomposition was described using an autocatalytic model [14]. Since all the above model fitting methods derive a single activation energy (E_a) for the process, reliable kinetic analysis could not be made as thermal decomposition involve multistep kinetics.

Most of the work on the thermal decomposition studies of GUDN was using classical Kissinger, Ozawa and ASTM methods. Heterogeneous solid state reaction can be better described using an isoconversional method. However, no work has been reported on the isoconversional kinetic studies of GUDN. In this work, the non-isothermal decomposition kinetics of GUDN has been studied by thermogravimetric analysis (TGA). Integral isoconversional method of Vyazovkin was used to investigate the dependence of activation energy (E_a) on conversion (α). E_a has also been determined for GUDN using Kissinger's method. The conversion as a function of time at two different temperatures was also predicted

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http://dx.doi.org/10.1016/j.tca.2016.03.019
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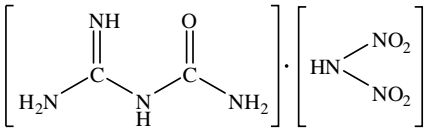

Fig. 1. Chemical structure of GUDN.

by a model free isoconversional approach. The decomposition products were identified by TG-MS. A mechanistic aspect and a comparison of results from these methods are also given in the paper.

2. Experimental

2.1. Materials and methods

GUDN was synthesized by a reported procedure. The detailed synthesis of GUDN can be found elsewhere [9–11].

TG experiments were carried out using a TA instruments SDT 2960 TG-DTA. Nonisothermal runs were performed at variable heating rates of 2, 3, 4 and 5 °C min^{-1} in the temperature range of 30–300 °C under nitrogen flow (100 mL/min). Samples were placed in open platinum pans. A sample mass of 1–2 mg were used for the nonisothermal experiments. The reproducibility of the TG signals was determined and there is practically no shift in the peak temperature when the heating rate and the mass of GUDN are kept the same. The mass effect was also studied, however a sample mass >3 mg produces a violent reaction generating a noise in the TG signal. Hence in our experiments the sample mass was kept below 2 mg.

GUDN showed a very sharp decomposition (narrow temperature range) without any melting. This has resulted in a sharp signal in a narrow temperature range as registered in the TGA. Several attempts have also been made to study the decomposition of this material at higher heating rates, however this has resulted in the sample being spurted out of the crucible at all times even though the sample mass is kept below 2 mg.

TG-MS analysis was done at a heating rate of 5 °C/min in helium atmosphere using PerkinElmer Pyris 1 TGA coupled with Clarus SQ 8T quadruple mass spectrometer through a heated fused silica transfer line. The transfer line temperature was maintained at 210 °C, and the evolved species were ionized in electron impact ionization mode with electron energy of 70 eV. Mass spectra of the evolved species were recorded for a mass range 10–500 amu. There is practically no time lag (time lag is less than 20 s) for most of the evolved species to reach the MS. But higher time lags are possible for species that may condense in the transfer line kept at 210 °C. In other words species with boiling points higher than the transfer line temperature can have a time lag, which is not applicable in this case.

Specific standards recommended by the supplier have been employed for the heat and temperature calibration of the instrument.

The data analysis and kinetic calculations from the TG measurements were done by using Microsoft ® EXCEL, Microcal ORIGIN® or OCTAVE® software [19].

3. Results and discussion

A typical TG-DTG curve of GUDN at a heating rate of 2 °C/min is shown in Fig. 2. Similar curves were obtained for all other heating rates. It is seen that GUDN undergoes decomposition in the temperature range of 180–225 °C leaving a residue of ~30% at 250 °C.

The characteristic decomposition temperatures of GUDN viz., initial temperature (T_o), peak temperature (T_p) (from DTG), and final temperature (T_f) at various heating rates are given in Table 1. The final temperature gives a clear indication of the completion of the decomposition reaction, and also the temperature difference between the initial and final values gives the temperature range of decomposition and Table 1 provides a summary of these events. It is seen from Table 1, that as the heating rate is increased, all the parameters got shifted to higher temperature as expected.

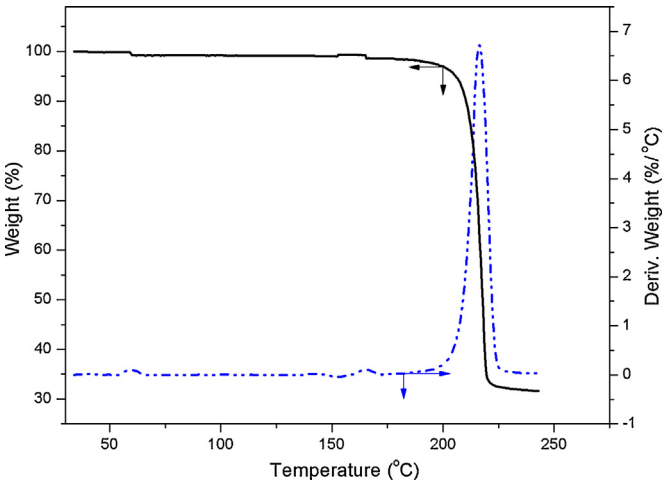

Fig. 2. TG-DTG curve of GUDN at a heating rate of 2 °C/min.

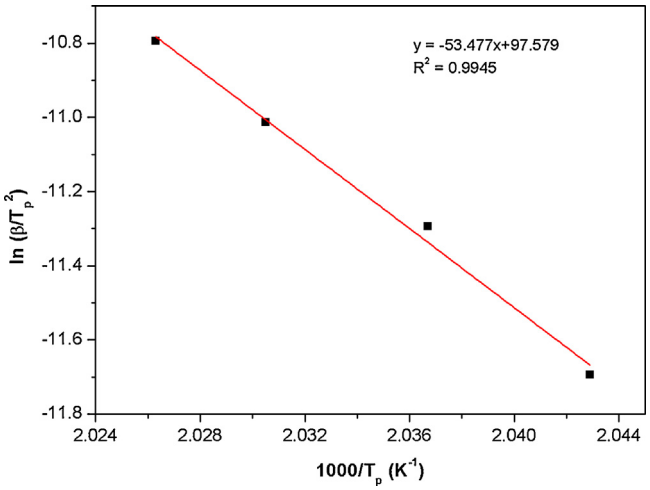

Fig. 3. Kissinger plot for GUDN.

3.1. Kinetic calculations

The basic equation for constant heating rate nonisothermal kinetic analysis is shown in Eq. (1).

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right) \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (1)$$

where T is the temperature, β is the linear heating rate, A is the pre-exponential factor, R is the gas constant, $f(\alpha)$ is the differential

Table 1
Characteristic temperature of decomposition for GUDN from TG.

H.R(°C/min)	T_o (°C)	T_p (°C)	T_f (°C)
2	179.8	216.5	227.1
3	182.4	218.0	230.0
4	184.8	219.5	233.2
5	187.3	220.5	235.5