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A Kinetics Investigation on the Nitro-Nitrite Rearrangement Mediated Thermal Decomposition of High Temperature Monoclinic Phase of 1,1-Diamino-2,2-Dinitroethylene (γ-Fox-7)

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Abstract. 1,1-Diamino-2,2-dinitroethylene (DADNE), commonly known as FOX-7, is one of the novel high energy density molecules recently developed along with CL-20, TNAZ and ADN. DADNE is well-known for its insensitive nature and this has motivated the research in understanding the thermal and explosive decomposition behaviour of DADNE. We have studied the thermal decomposition kinetics of DADNE employing two isoconversional methods *viz.*, Friedman's differential method and Vyazovkin's non-linear integral method. For the study, Differential Scanning Calorimetry as well as Thermogravimetry data collected at lower heating rates ($<5°C/min$) were used. This study indicated a four stage decomposition behaviour of DADNE, where each stage is characterised by different activation energy. Computed activation energy values have been used to understand the thermal decomposition mechanism of DADNE.

Keywords. FOX-7; Decomposition kinetics; isoconversional kinetics; activation energy; decomposition mechanism

1. Introduction

1,1-Diamino-2,2-dinitroethylene (DADNE, FOX-7) is considered as one of the most promising energetic materials because of its insensitive nature. Since the first successful synthesis of DADNE reported in 1998,[1] there has been a number of methods reported in the literature and some of them deal with the large scale production of DADNE.[2-4] Being a potential insensitive energetic material, thermal decomposition kinetics and mechanism of DADNE has attracted the interest of researchers, and many theoretical[5-11] and experimental reports have been published till date.[12-14] A better insight into the decomposition mechanism of DADNE will enable us to understand the decomposition phenomena of structurally similar energetic molecules such as 2-(dinitromethylene)imidazolidine-4,5-dione, 2-(dinitromethylene)-5,5-dinitropyrimidine-4,6-(1H,3H, 5H)-dione, Triaminotrinitrobenzene (TATB), Tetranitroacetimic acid (TNAA), etc., containing amino and nitro groups.

Owing to the applications and hazardous nature of energetic materials, understanding their thermal decomposition behaviour and kinetics has a long known demand.[15,16] Though the thermal decomposition

behaviour and kinetics of DADNE has undergone many investigations, most of these studies are theoretical in nature[5-11] and a few are experimental studies.[12-14] However, no experimental studies were conducted to understand the low temperature decomposition behaviour or to correlate the available theoretical information with experimental studies. Hence, in the present study attempts are made to understand the variation of E_α with respect to different stages of decomposition of DADNE at lower heating rates ($<5°C/min$) and tried to correlate the theoretical information available and draw mechanistic conclusions about the decomposition process. Friedman's differential isoconversional method and Vyazovkin's non-linear integral isoconversional method were used to compute the activation energy of the decomposition process.

A detailed literature survey showed that four major decomposition pathways were reported[5-14] for the thermal decomposition of DADNE and these are represented in Schemes 1–4. All the pathways suggest either NO, NO_2 or NO_3 is fragmented through O–N or C–N bond cleavage. The bond enthalpy of N–O being $157 \, kJ \, mol^{-1}$ and that of C–N bond being $305 \, kJ \, mol^{-1}$, the thermodynamics favours the cleavage of N–O bond and subsequent release of NO as per the Scheme 1. However, the possibilities of resonating structures make decomposition a complex process with different stages.
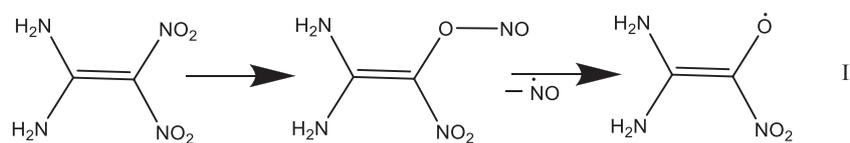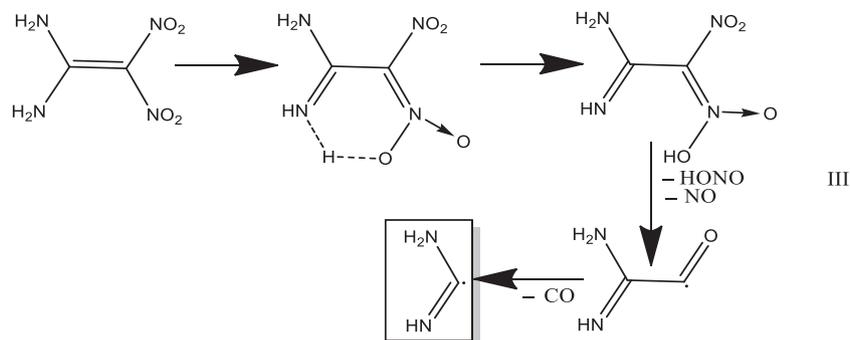
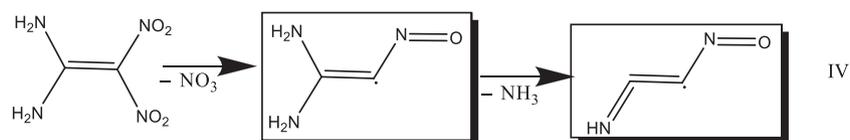**Scheme 1.** Decomposition pathway I.
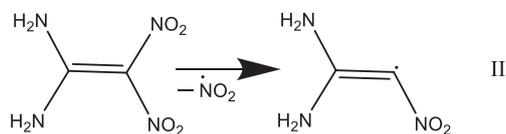
Scheme 2. Decomposition pathway II.

Scheme 3. Decomposition pathway III.

Scheme 4. Decomposition pathway IV.

To get more insights into the complex decomposition mechanism, the kinetics of decomposition process are investigated. Isoconversional method of kinetic analysis was used to understand the dependence of the activation energy (E_α) on the extent of conversion (α). The isoconversional methods employ multiple heating rates to obtain data on varying rates at a constant extent of conversion. Detailed description of the isoconversional kinetic analysis is given in the International Confederation for Thermal Analysis and Calorimetry (ICTAC) recommendations.[17] α can be computed either from the mass loss data obtained from TGA runs or heat release data obtained from DSC runs. As the method considers the kinetics of the process by using multiple single-step kinetic equations,[17] the isoconversional methods of kinetic analysis permit to explore the multistep kinetics of the thermal decomposition reactions (or any thermally stimulated process) and help in drawing mechanistic conclusions about the process under investigation[18,19] and even to determine the thermal stability of material under investigation.[20] As the method tracks the changes in E_α throughout the entire decomposition process, it allows a more accurate kinetic assignment of the individual steps of complex decompositions.[19] Based on the Arrhenius equation, alternative kinetic equations can be derived and many methods make use of this principle. However, a few methods are very popular in the literature, namely, Flynn-Wall-Ozawa's linear integral method,[21,22] Friedman's differential method[23] and Vyazovkin's non-linear integral method,[24] which is a recent one. Being a differential method, the Friedman method offers an advantage, however, the method uses instantaneous rate values which are quite susceptible to experimental noise, leading to larger variations in E_α values.

Earlier studies[12–14] report activation energy values in the range of 198–372 kJ mol^{-1} and these are tabulated in Table 1. In this paper, variation of E_α with α is traced

Table 1. Average activation energy values reported for DADNE in literature.

Activation Energy (kJ mol^{-1})	Method
372.3[12]	Kissinger
326 ± 28.7[12]	Modified Flynn-Wall-Ozawa
334.5 ± 22.9[12]	Friedman
198[13]	From volume of gaseous products
234[14]	ASTM E698-99

and an attempt is made to correlate this information with the reported theoretical postulates.

2. Experimental

2.1 *Material and methods*

The DADNE used in the present study was kindly provided by High Energy Materials Research Laboratory (HEMRL), Pune, India, and the material was used as received without any further purification.

2.2 *Thermal analysis*

DSC analysis was carried out on a Perkin Elmer DSC8000 instrument. The samples were loaded into a closed aluminium pan and heated under nitrogen flow maintained at 40 mL/min. The TG-DTA experiments were performed on a TA instrument Q600 SDT under flowing nitrogen atmosphere of 100 mL/min.

2.3 *Phase transition studies*

The DADNE sample was thermally cycled at $\beta = 5°C/min$, from 50 to 200°C and the cycling sequence was 50–200°C → 200–50°C → 50–200°C → 200–50°C. The sample was held for 2 min at the isothermal condition at the final temperatures before reversing the temperature (The thermal cycling data are given as Supplementary Information). Further, about 10 mg of DADNE was non-isothermally heated in an open alumina crucible at 2.5°C/min heating rate (β) up to 200°C and isothermally held at 200°C for 30 min. The sample was cooled down to room temperature (in ∼30 min) and used for Powder X-ray (PXRD) analysis.

2.4 *Decomposition kinetic analysis*

Two model-free (isoconversional) methods, namely Friedman's differential method[23] and Vyazovkin's non-linear integral method[24] were employed for the kinetic analysis. The third degree approximation proposed by Senum and Yang[25] was used in the present study to evaluate the integral by the non-linear integral method. An α interval of 0.01 was used to compute the E_α from TGA data as well as DSC data using the isoconversional methods.

2.4a *Extent of conversion (α)*: The nonisothermal DSC experiments were conducted at heating rates (β) 2.5, 3.5 and 4.5°C/min. Extent of conversion was computed by striping the area under the DSC curve (ΔH) into smaller regions and dividing each segment by the total area under the curve (ΔH). A MATLAB code based on trapezoidal numerical integration method was used to convert the area under the curve into α. In all the DSC experiments, less than 1.5 mg of sample was loaded and heated. Further, for a better understanding of the decomposition behaviour and dependency on the heating rate, the DSC data was collected at 10°C/min. The nonisothermal TG runs were conducted at heating rates (β) 1.5, 2.5, 3.5 and 4.5°C/min and the obtained data were converted to α using the standard equation $\alpha = (m_0 - m_t)/(m_0 - m_f)$; where, m_0 is the initial mass, m_f is the final mass and m_t is the mass at a given temperature. In all the TG experiments, 1–1.4 mg of sample was loaded in an open 90 μL alumina pan and heated.

Two isoconversional methods, namely, Friedman method and Vyazovkin method were employed for the kinetic analysis. The theoretical background of kinetic analysis is given as Supplementary Information.

3. Results and Discussion

3.1 *Phase transition studies*

Different crystallographic phases and possibilities of phase transition are reported in the literature,[26] however, present DSC data obtained at 2.5°C/min (Figure 1) showed a phase transition at 118°C and another transition at 179°C. Further, about five milligram sample was heated to 200°C and held at the temperature for 30 minutes. The sample was then cooled down to room temperature and analysed using PXRD. PXRD reflections of heated DADNE sample was then compared with the PXRD reflections of pure DADNE and the data is shown in Figure 2. The data showed that the phase is the same before heating the sample to 200°C. After the transition at 179°C, the molecule started decomposing, indicating that the decomposing phase is high-temperature monoclinic phase.
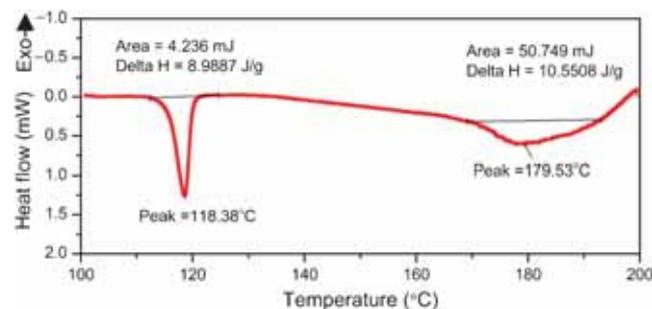
Figure 1. DSC trace of DADNE at $\beta = 2.5°C/min$.
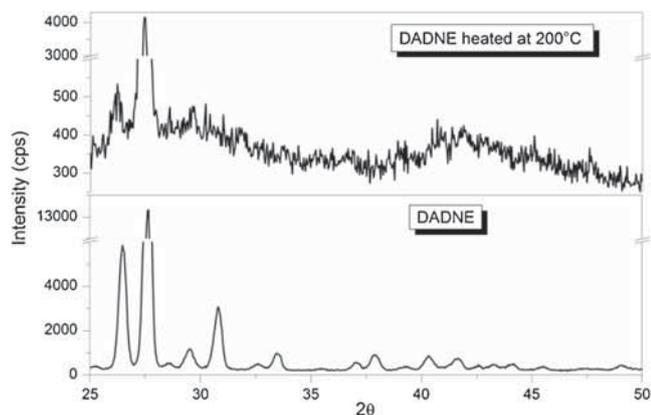
Figure 2. PXRD pattern of DADNE before and after thermal treatment.

3.2 *Thermal Decomposition by DSC*

The DSC data obtained at 2.5 and 10°C/min heating rate is shown in Figure 3a. Most of the earlier studies report the TG/DSC collected at heating rate of 10°C/min. However, in the present study, the molecule was found to follow two different decomposition pathways at lower and higher heating rates, though the major decomposition of the molecule occurs close to 280°C. In fact, the decomposition stages below 260°C (excluding the major decomposition peak) shown in Figure 3b indicate the different stages in the decomposition process when heated at different heating rates.

3.3 *Thermal decomposition by TG*

The TG analysis of DADNE was carried out at different heating rates and the behaviour observed at heating rate of 2.5 and 10°C/min are shown in Figure 4. In the four stage decomposition exhibited by DADNE at 2.5°C/min heating rate, the first stage decomposition

accounts for 3% of initial mass, while second stage 16% (13%), third stage 40% (24%) and fourth stage 83% (43%) of the initial mass, where the values in bracket indicate the difference of percentage decomposition from the previous step. As can be seen in the figure, the rate of mass loss denoted by DTG (first derivative of the TG data) curve (Figure 4), is highest for the fourth stage and consequently the rate of reaction. The other three stages have a very low mass loss rate, in fact, the rate is less than half of the fourth stage.

3.4 *Kinetic analysis*

3.4a *From DSC data*: For kinetic analysis, the DSC heat flow curves obtained at three different heating rates 2.5, 3.5 and 4.5°C/min were used. Similar to the four stage decomposition behaviour exhibited by TG analysis, the DSC analysis also exhibited four stage decomposition. As explained, the E_α values for the DADNE decomposition was calculated and shown in
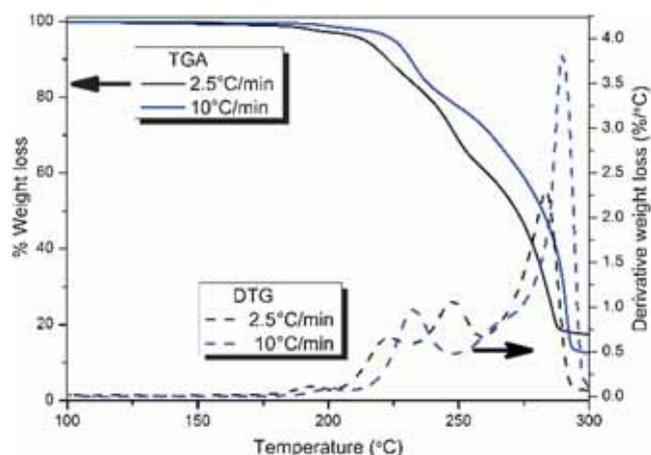

Figure 4. TG-DTG curve of DADNE decomposition obtained at different heating rates.
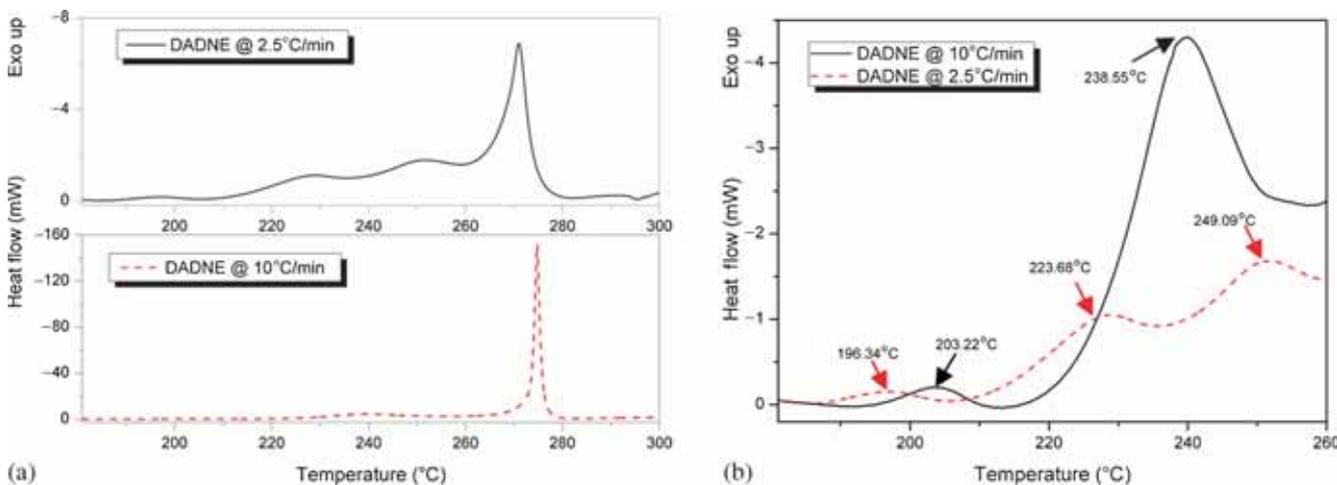

Figure 3. a) DSC trace of DADNE decomposition; b) Comparison of DADNE decomposition at different heating rates.

Figure 5. The E_α showed a dependency on the α, indicating different stages of decomposition and the average E_α value was $\sim$154 kJ mol^{-1}. Interestingly, different stages of decomposition were defined by different activation energy values. The last stage decomposition was defined by an average activation energy of 152 kJ mol^{-1}. Though the E_α value decreased till $\alpha = 0.7$, it started increasing after this point, possibly indicating a decrease in the reaction rate. The activation energy computed by nonlinear integral isoconversional method is submitted as Supplementary Information.

To get more insight into the different stages of decomposition and the activation energy demanded by individual stages, the E_α and Heat flow (@ 2.5°C/min) was plotted against α and shown in Figure 6. As expected, the E_α variation was in line with the different stages of decomposition.
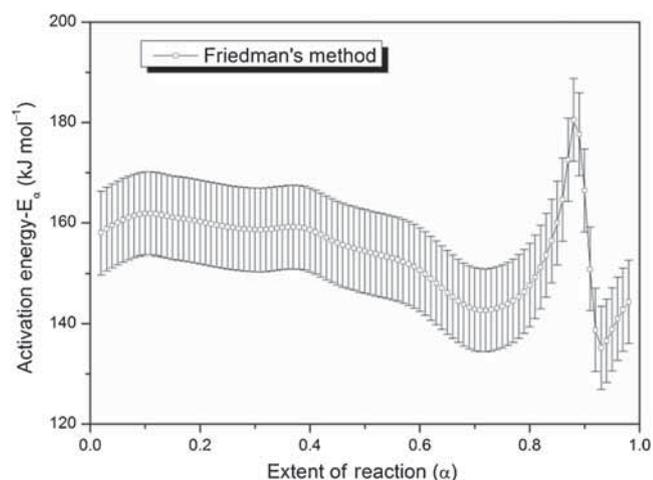
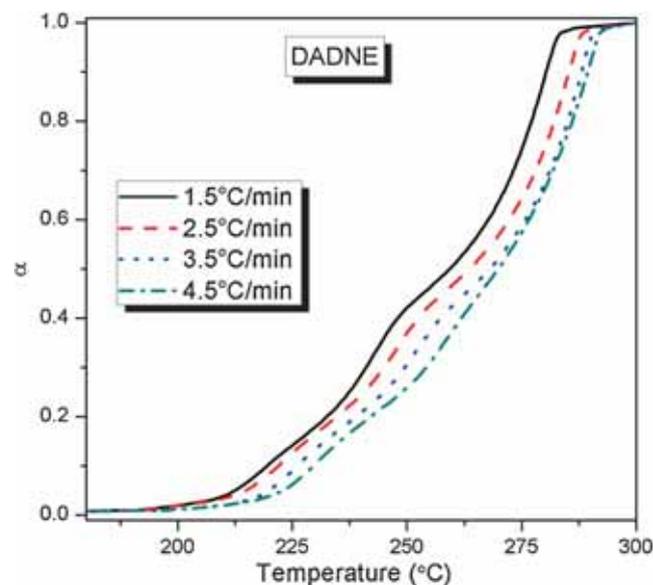**Figure 5.** Variation of activation energy with extent of conversion (from DSC data).
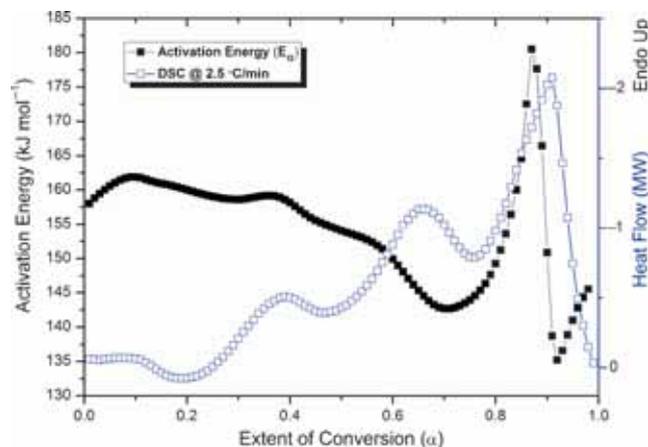
Figure 6. Variation of activation energy and heat flow ($\beta = 2.5$°C/min) with extent of conversion.

3.4b From thermogravimetric analysis data: Initially, the thermal decomposition/mass loss curves were recorded at four different heating rates 1.5, 2.5, 3.5 and 4.5°C/min. As shown in Figure 7, the TG data were converted to α and plotted against temperature, and the kinetic curves too exhibited a four stage decomposition. Even though, the decomposition exhibited four different stages, the dependency behaviour of E_α with α was different from that obtained from DSC data (Figure 8). The average activation energy stood at a higher value of 254 kJ mol^{-1}. However, after reaching $\alpha = 0.15$, a lowering of E_α was observed. Usually this behaviour is interpreted as slow down of the decomposition process. But, in the present situation this does not actually correspond to a slowdown, because, the mass loss rate tends to increase from a lower value to higher values and it never comes down to 0% mass loss rate. So this phenomenon indicates the actual lowering of E_α required for the second stage decomposition. The activation energy computed by nonlinear integral isoconversional method is submitted as Supplementary Information.

Similar to the DSC data, the E_α and DTG are plotted against α and shown in Figure 9, the plots indicated different activation energy for different stages.

3.5 Discussion of Results

The phase transition in DADNE, especially the lesser known $\beta \rightarrow \gamma$ transition has been well-studied in a recent paper and established the crystal structure.[27] In the present study, to understand the decomposing phase,

Figure 7. α - T kinetic curve for DADNE decomposition (from TG data).
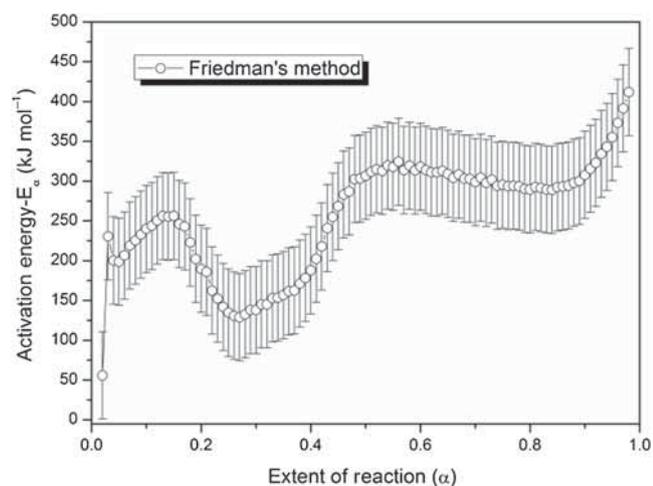
Figure 8. Variation of activation energy with extent of conversion (from TGA data).
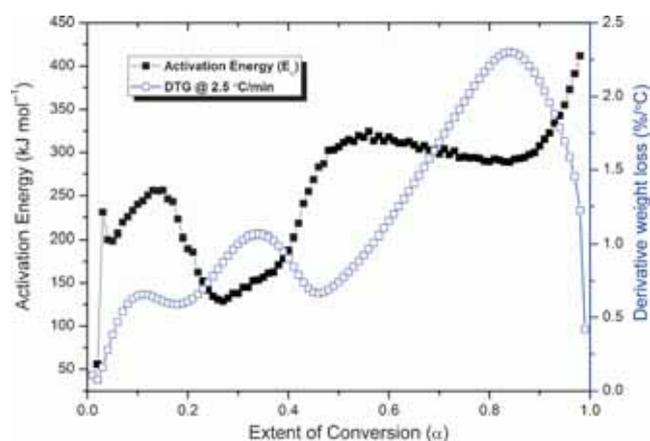

Figure 9. Variation of activation energy and weight loss rate ($\beta = 2.5°C/min$) with extent of conversion.

we have carried out the phase transition studies and confirmed that the monoclinic phase occurring above 175°C decomposes immediately after the phase transition. Though the $\beta \rightarrow \gamma$ transition did not appear as a well-defined endothermic peak, the literature showed that the roughness of the DSC curve during the $\beta \rightarrow \gamma$ transition is likely to be a consequence of the "thermosalient effect", which causes crystals to undergo a phase transition to "jump" or "hop." In some cases, crystals are reported to jump by nearly 0.30 m.[28] Detailed analysis of this observation in DADNE crystals by earlier researchers[27] ascertains that during the $\beta \rightarrow \gamma$ transition several crystals jumped. However, when the DADNE sample was analysed by DTA, the roughening of the curve was not observed, instead a broad peak centred at 174°C was observed. Possibly, the less sensitive nature of the DTA technique and the fact that samples are placed in an open alumina holder have led to such behaviour.

Immediately after the $\beta \rightarrow \gamma$ transition, the DADNE started decomposing and the behaviour was confirmed by both DSC and TG/DTA studies. The samples exhibited four different stages of decomposition at lower heating rates and three stage decomposition at higher heating rates. The decomposition stages with less ΔH and dm/dT was revealed because of the higher resolution offered by the lower heating rates. In literature, the studies were carried out at heating rates close to 10°C/min and at this rate the DADNE showed two stage decomposition above 220°C. In DSC and DTA, all the decomposition peaks appeared as exothermic and the peak observed at 223°C was found to merge with the next stage at higher heating rates.

Theoretical studies on the thermal decomposition behaviour of DADNE reported by different researchers postulate different decomposition pathways.[5-11] However, none of the theories are explicitly supporting the experimental data obtained in the present study or even earlier studies. The activation energy calculated from DSC data showed four different regions. The average activation energy for the first stage was 160 kJ mol^{-1}, second stage was 158 kJ mol^{-1}, third stage 148 kJ mol^{-1} and the fourth stage 152 kJ mol^{-1}. Though the activation energy showed a dependency on the α, it remained close to 95% confidence interval range, *i.e.*, 152.6 to 156 kJ mol^{-1}. This probably indicates the possible simultaneous occurrence of different processes, while the rate determining step remains to be the same. The complete decomposition reaction of DADNE produces H_2O, CO and N_2, as shown in Scheme 5.[13]

In the TGA based kinetic analysis, the first stage accounts only for an α value of 0.02 and assigning the E_α values for this process would be erroneous and no attempt is made for the same. The second stage is described by an average activation energy of 209 kJ mol^{-1}, third stage with an average activation energy of 247 kJ mol^{-1} and the fourth stage by 311 kJ mol^{-1}. The 95% confidence interval of the data was 242.4 to 270.60 kJ mol^{-1}. Earlier quantum chemical calculations suggested first step of the thermal decomposition is the loss of HNO_3, H_2O, NO_2[29] or NO.[11] Interestingly, experimental activation energy values matched closely with the theoretically reported activation energy[5,9] for the processes shown in Schemes 1 and 3, respectively.
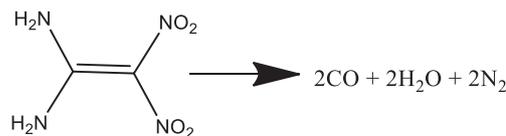
Scheme 5. Decomposition pathway V.

These observations quite possibly indicate the co-existence of different pathways at different stages with slightly varying ratios. In fact, an initial attempt was made to compute the kinetic parameters for DADNE decomposition, using the TGA data collected at higher heating rates, employing the isoconversional method. However, the TGA data collected at 5, 7.5, 10 and 12.5°C/min were not obeying the isoconversional principle, "the reaction rate at constant extent of conversion is only a function of temperature and hence the reaction model is not dependent on heating rate". Also, one of the earlier Mass Spectrometry based decomposition studies on DADNE,[29] where the heating rate used was relatively high, only three major species were observed and reportedly follows the Scheme 4. The fragments obtained in the previous experimental studies are highlighted as boxes in the schemes. More likely, these processes that occur simultaneously at different rates with different activation energy will contribute to the apparent activation energy values obtained by the isoconversional method.

Understandably, the confusing character of the kinetic information is due to different chemical and physical process such as solid-state decomposition, gas-phase reactions of the decomposition products and physical process like diffusion, sublimation, etc. Reasonably, the effective activation energy of the thermal decomposition is determined by the contribution of individual process and their relative contribution to the overall reaction rate. Hence, it may be concluded that in DSC at lower heating rates, intramolecular hydrogen transfer, likely resulting in the production of reactive radical intermediates and HONO (Scheme 3), is the rate determining step.

In the present study the DSC and TG based kinetic analysis yielded different E_α values. The reason for this change can be attributed to the open (in TGA) and closed (DSC) environment during the experiments. This behaviour is not new and this has been extensively studied and reported in the case ammonium perchlorate.[30] The samples are in a sealed condition in the DSC crucibles and this increases the possibility of secondary reactions. In DSC, the fragments will interact with left over DADNE leading to secondary reactions changing the heat flow and subsequently the activation energy values. While in the case of TG analysis, the decomposed fragments are carried away by the purge gas (N_2) from the partially decomposed DADNE sample and this minimizes any possibility of secondary reactions. This has apparently led to the change in the E_α values calculated using data from different experiments.

The previous studies reported an average activation energy of 334.5 ± 22.9 kJ mol^{-1} using Friedman method, while the present study reports 256 ± 70.36 kJ mol^{-1}. The difference might have originated from the initial data collected for the kinetic analysis which is different in both the cases. The sample mass also known to affect the collected data and therefore, ~ 1 mg sample is preferred in most of the cases. Also, it was shown that the DADNE undergoes different pathways at lower and higher heating rate and the data collected at higher heating rate was not obeying the isoconversional principle. Hence, cumulative effect of these differences would have resulted in discrepancies with the previous reported values. Another point worth mentioning is the applicability of the isoconversional method to determine the kinetics of multi-step processes by using multiple single-step kinetic equations; it permits to explore the kinetics of the multistep thermal decomposition reactions, which is utilized in the present study.

4. Conclusions

At lower heating rates, DADNE exhibits a four stage decomposition. The kinetic study indicates that many decomposition pathways co-exist during the thermal decomposition of DADNE. The kinetic parameters computed using DSC data indicate that the rate determining step which proceeds through the production of NO and HONO dominates throughout the process. While the kinetic parameters computed using TGA data indicate the possibility of each decomposition stage having many simultaneous reactions. Also, each individual process was found to contribute to the apparent activating energy observed at a given extent of conversion. The effective activation energy of the thermal decomposition of DADNE is obviously a composite value determined by the activation energies of elementary steps as well as by the relative contributions of these steps to the overall reaction rate.

Supplementary Information (SI)

The theoretical background of kinetic analysis, thermal cycling data of DADNE, phase transition data by TGA, DSC traces of DADNE decomposition and activation energy calculated by nonlinear integral isoconversional method are given as Supplementary Information. Supplementary Information is available at www.ias.ac.in/chemsci.

Acknowledgements

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