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Research paper

Investigation of the Thermal Stability and Triple Kinetic Calculation of the Decomposition Temperature of 3-Azido-2,2-bis(azidomethyl)propyl azidoacetate as an Energetic Plasticizer using Model Free Methods

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Abstract: The energetic plasticizer 3-azido-2,2-bis(azidomethyl)propyl azidoacetate (ABAMPA) can be employed in double-base propellant formulations due to its efficacy. The thermal properties of ABAMPA were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Non-isothermal DSC measurements at heating rates of 2, 5, 10 and 15 K/min revealed that the exothermic decomposition temperature of ABAMPA ranges from 221.48 to 254.93 °C. Further investigation involved analyzing ABAMPA's thermal decomposition kinetics through non-isothermal methods like Kissinger and Flynn-Wall-Ozawa (FWO), offering a critical understanding of its thermal behaviour and potential enhancement in propellant applications. The activation energy, frequency factor and rate constant of the decomposition temperature of ABAMPA were found to be 121.18/123.31 kJ mol⁻¹, 7.56×10¹¹/ 1.27×10¹² s⁻¹ and 4.45×10⁻¹⁰/3.17×10⁻¹⁰ s⁻¹, respectively at 298 K, using the Kissinger/FWO methods. Critical temperatures for ABAMPA were assessed as 218.25 °C (based on ASTM data) and 218.36 °C (according to FWO data). The Kissinger method predicted a half-life of approximately 22.05 years, whereas the FOW method yielded a value of around 30.52 years. In addition the thermodynamic parameter values for the transition state of ABAMPA during thermal decomposition were derived from the Kissinger and FOW methods. The results of this work confirmed the good thermal stability of ABAMPA as an energetic plasticizer.

Keywords: 3-azido-2,2-bis(azidomethyl)propyl azidoacetate, ABAMPA, thermal stability, Kissinger, Flynn-Wall-Ozawa, non-isothermal kinetics

Supplementary Material

Figures of the IR, ^1H and ^{13}C NMR spectra of 3-azido-2,2-bis(azidomethyl)propyl azidoacetate, ABAMPA, are available in Supplementary Information.

1 Introduction

Plasticizers play a critical role in explosive and propellant formulations, serving as essential components that enhance both safety and mechanical performance [1-3]. Plasticizers are frequently employed in propellants to improve their mechanical properties. Their incorporation reduces the viscosity, facilitates processing and extends the pot life of propellant formulations [1, 4]. Plasticizers are introduced into polymers to reduce stiffness by modifying the polymeric matrix and weakening the strong cohesive interactions between adjacent polymer chains. Additionally, they enhance the mobility of segments by increasing the free volume within the structure. Such expanded spatial distribution of unbound molecules ultimately lowers the glass transition temperature (T_g) of the material. The extent of T_g depression induced by a given plasticizer is commonly taken as a measure of its efficiency [4, 5]. Both inert (non-energetic) and energetic plasticizers are employed in explosive and propellant formulations [6, 7]. Energetic plasticizers are characterized as liquid compounds with a positive heat of formation, playing a critical role in increasing the energy output of the system. Additionally, they enhance flexibility and elasticity, making them preferable to non-energetic plasticizers [8]. Structurally, these plasticizers typically contain functional groups such as nitro, difluoroamino, nitramino, and azido within their molecular frameworks [6, 9].

The ester group exhibits excellent lubricating properties, while azido ester plasticizers display remarkable compatibility with common energetic binders in solid propellants, notably azido and nitrate ester binders. Furthermore, these plasticizers possess several advantageous characteristics, including low vapour pressure, high boiling point, reduced viscosity, and excellent processability. Notably, the introduction of azido plasticizers into propellant formulations significantly reduces smoke emission, enhancing both energy conversion efficiency and thermal safety [4, 10]. Another crucial consideration is the influence of an azido plasticizer on a system's energy level, which stems from the favourable enthalpy of formation characteristic of the N_3 group [11]. Thermal stability analysis of energetic plasticizers is essential for assessing their safety

during formulation, handling and storage. Such investigations also provide valuable data regarding shelf life and thermodynamic parameters of chemical decomposition [12, 13].

Azido-ester plasticizers provide enhanced decomposition energy and significantly reduce smoke emission, while maintaining excellent compatibility. Their primary decomposition product is N_2 gas, which is environmentally friendly and non-toxic, thereby ensuring smokeless combustion [13, 14].

3-Azido-2,2-bis(azidomethyl)propyl azidoacetate (ABAMPA) is an energetic plasticizer with a suitable T_g and low sensitivity to external stimuli such as impact and friction, making it a promising candidate for propellant formulations. In the present study, the thermal stability of ABAMPA was investigated for the first time, and its triple kinetic parameters of thermal decomposition were determined using model free methods. Furthermore, the thermodynamic parameters of ABAMPA's chemical decomposition were calculated and its shelf life was estimated.

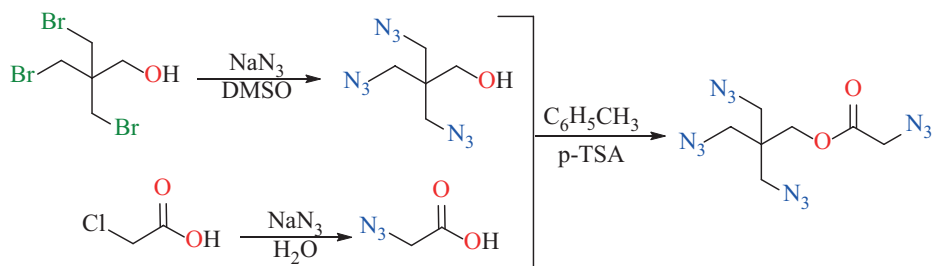
2 Experimental

2.1 Materials and methods

All reagents and solvents used in this study are commercially available and were purchased from commercial suppliers (Acros, Merck and Aldrich). A Nicolet 800 spectrometer was used to record the FT-IR spectra. A Bruker DPX-250 instrument operating at 300 MHz was used to record the NMR spectra and chemical shifts are reported in δ (ppm) from TMS. The thermal behaviour of the sample was analyzed using PerkinElmer STA 6000 equipment, with alumina pans under N_2 atmosphere, through thermogravimetric (TG) and differential scanning calorimetric (DSC) analyses. The temperature was programmed to increase at a rate of 2, 5, 10, or 15 K/min from room temperature to 450 °C, and the sample masses were 2.5 mg.

2.2 Synthesis of ABAMPA

ABAMPA was synthesized according reference [3] with some modification. Using 3-bromo-2,2-bis(bromomethyl)propan-1-ol as a starting material, ABAMPA was synthesized through a three steps reaction (Scheme 1). 3-Bromo-2,2-bis(bromomethyl)propan-1-ol was reacted with sodium azide (NaN_3) to produce 3-azido-2,2-bis(azidomethyl)propan-1-ol. Also, 2-azidoacetic acid was obtained by azidation of 2-chloroacetic acid with NaN_3 . The 3-azido-2,2-bis(azidomethyl)propan-1-ol was then reacted with the 2- azidoacetic acid in toluene in presence of *p*-toluenesulfonic acid (*p*-TSA).



Scheme 1. Synthesis route to ABAMPA

3 Results and Discussion

3.1 Spectral analysis

To confirm the structure of ABAMPA, FT-IR and NMR techniques were employed. As shown in Supporting Information (SI), in Figure S1, the structure of ABAMPA could be easily verified by FT-IR spectroscopy. The FT-IR spectrum displayed a strong stretching bands at 1750 cm^{-1} for C=O, and 2099 cm^{-1} for N=N=N, which indicated the successful condensation reaction of 3-azido-2,2-bis(azidomethyl)propan-1-ol with 2-azidoacetic acid.

The ^1H NMR spectrum of ABAMPA showed peaks at 4.08 (2H, s, CH_2O), 3.92 (2H, s, CH_2N_3), and 3.37 (6H, s, CH_2) ppm (SI, Figure S2). Furthermore, the ^{13}C NMR spectrum revealed peaks at 168.14, 64.72, 51.72, 50.76, and 43.74 ppm (SI, Figure S3). These results confirmed the structural features of ABAMPA and its successful synthesis.

3.2 Thermal study

The DSC curves of ABAMPA samples, recorded at heating rates of 2, 5, 10, and $15\text{ K}\cdot\text{min}^{-1}$, from room temperature to $450\text{ }^\circ\text{C}$, are illustrated in Figure 1. As shown in Figure 1, the exothermic peak of ABAMPA appeared within the temperature range of approximately $221.5\text{--}259.7\text{ }^\circ\text{C}$. As the heating rate was increased, the decomposition temperature of ABAMPA shifted to higher temperatures. These observations were subsequently utilized to determine the thermokinetic parameters of the decomposition process.

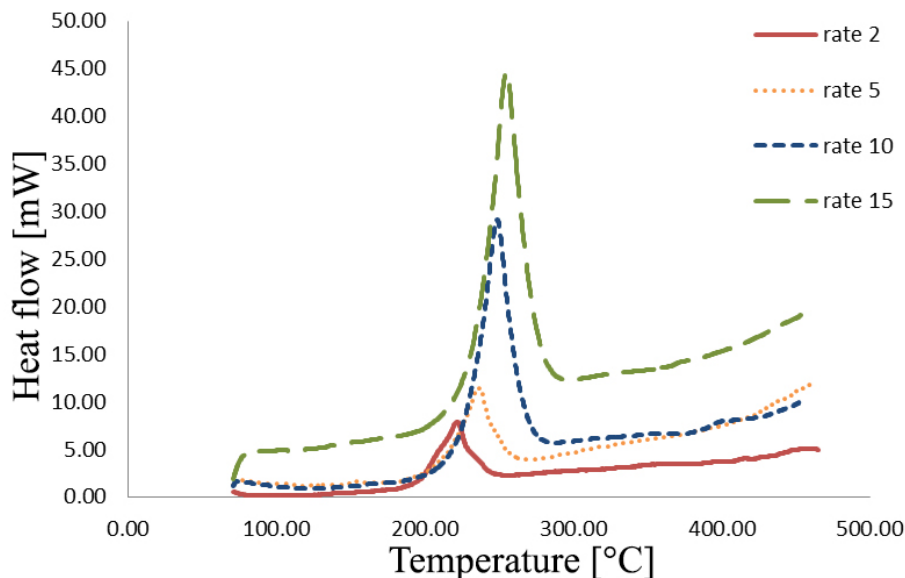


Figure 1. DSC thermograms of ABAMPA samples at various heating rates (2, 5, 10 and 15 K·min⁻¹)

The DSC technique was employed to evaluate the thermal stability and activation energy of ABAMPA decomposition. Figure 2 shows the thermogravimetric (TG) curves of ABAMPA under a nitrogen atmosphere, illustrating its thermal behaviour at elevated temperatures. The TG curves reveal a single stage mass loss process, with initial decomposition beginning at approximately 170 °C and being complete by 250 °C, and resulting in a total mass loss ranging from 68.60 to 81.09%. Kinetic analysis of the exothermic decomposition reactions of energetic materials is critically important for assessing their thermal stability, long-term storage safety, and associated handling risks. DSC is widely employed to determine the kinetic parameters of such decomposition reactions. DSC analysis of ABAMPA revealed a decomposition enthalpy of 1750.89 J/g. (See Figure S4 in SI). The relatively high magnitude of this exothermic enthalpy of decomposition confirms the presence of substantial chemical energy stored within the compound's molecular structure. In this study, non-isothermal DSC measurements were utilized to investigate the thermal decomposition kinetics of ABAMPA.

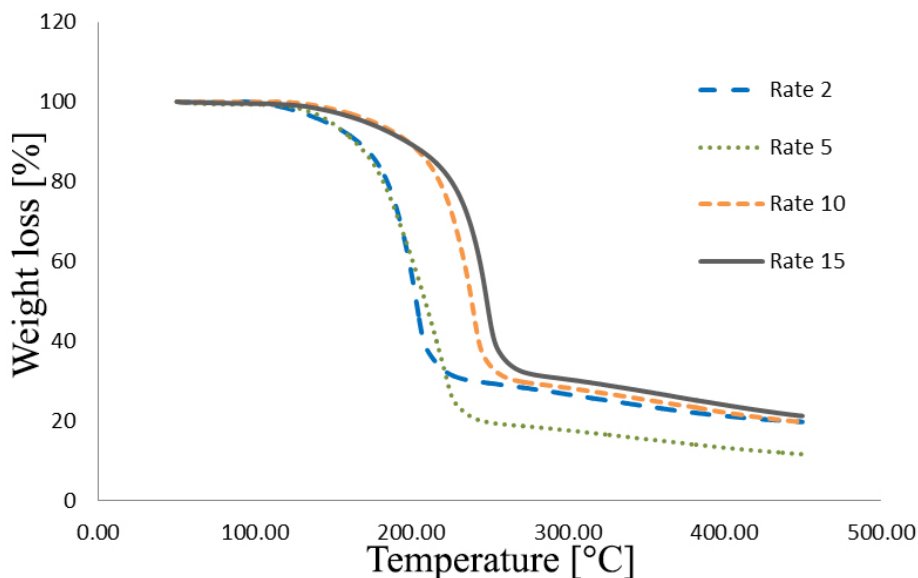


Figure 2. TG thermograms of ABAMPA samples at various heating rates (2, 5, 10, and 15 K·min⁻¹)

For evaluating the decomposition kinetics from the DSC thermograms, the model-free analysis methods of the Kissinger and the Flynn-Wall-Ozawa (FWO) approaches were utilized. These well-established methodologies were employed to calculate the activation energy and other kinetic parameters without assuming specific reaction models, following current best practice in thermal analysis of energetic materials.

3.3 Methods for the determination of the activation energy and frequency factor

Several analytical techniques are available for determining the activation energy. Among these, model free iso-conversional methods stand out as particularly robust approaches for calculating the activation energy. Notably, the Kissinger and the FWO methods are widely employed to estimate the activation energy based on thermal analysis data.

The Kissinger method is a widely used technique for determining the activation energy of decomposition reactions of energetic materials. In the present study, which focused on elucidating the thermal stability and safety of ABAMPA, particular emphasis was placed on calculating the activation energy relevant to its thermal decomposition process. Harnessing the discriminating

power of non-isothermal DSC, the Kissinger method was selected as the primary approach. This enabled an accurate estimate of ABAMPA's activation energy, thereby giving a comprehensive understanding of its intrinsic thermal properties. The results obtained from this study provide essential information for evaluating the safety and stability of ABAMPA, emphasizing the significance of kinetic analysis in assessing energetic materials [14, 15].

DSC measurements were carried out at four different heating rates, 2, 5, 10 and 15 K·min⁻¹. The resulting DSC curves exhibited exothermic decomposition peaks at different temperatures, which were dependent on the heating rate. The Kissinger method was employed to determine the activation energy by plotting $\ln(\beta/T_p^2)$ versus $1000/T$, where T is the peak temperature of the exothermic decomposition in the DSC curve, β denotes the corresponding heating rate (K·min⁻¹), and R is the universal gas constant (8.3145 J mol⁻¹K⁻¹). Equation 1 was used for this calculation:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{T}\right) - \frac{E_a}{RT_p} \quad (1)$$

According to Kissinger's method, the activation energy (E_a) can be determined by plotting $\ln(\beta/T_p^2)$ versus $1/T_p$ and calculating the slope of the resulting linear relationship using Equation 1. Applying this approach, the activation energy was estimated to be approximately 121.18 kJ/mol. Table 1 lists the complete dataset used for this calculation, including all heating rates and the corresponding peak temperatures.

Table 1. Calculation of activation energy for ABAMPA decomposition using the Kissinger method

| β [K/min] | T_p [K] | $1/T_p \times (10^3)$ | $\ln(\beta/(T_p)^2)$ |
|-----------------|-----------|-----------------------|----------------------|
| 2 | 494.63 | 2.021713 | -11.7145 |
| 5 | 509.24 | 1.963711 | -10.8564 |
| 10 | 521.67 | 1.916921 | -10.2115 |
| 15 | 528.08 | 1.893652 | -9.83045 |

The activation energy of the reaction was thus determined. Under the assumption of first-order kinetics, the pre-exponential factor was calculated according to the approach outlined in reference [16].

$$Z = \beta E_a \exp\left(\frac{E_a}{RT_p}\right) / (RT_p^2) \quad (2)$$

where β represents the heating rate (in $\text{K}\cdot\text{min}^{-1}$), E_a is the activation energy (in $\text{kJ}\cdot\text{mol}^{-1}$), R denotes the universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), A stands for the pre-exponential factor (in s^{-1}), and T_p indicates the peak temperature (in K).

In addition to the Kissinger method, a second approach was employed to compare the activation energy and frequency factor values. Based on the mathematics of heterogeneous chemical reactions, Flynn, Wall, and Ozawa (FWO) developed a kinetic analysis method for determining kinetic parameters from TG and DSC data. The FWO method is based on the isoconversional principle, which states that the reaction rate at constant conversion depends solely on temperature. The governing equation of the FWO method is as follows [17, 18]:

$$\log \beta = \log \left(\frac{AE_a}{RG(\alpha)} \right) - 2.315 - 0.4567 \frac{E_a}{RT} \quad (3)$$

At the maximum peak temperature, the degree of conversion (α) remains constant regardless of variations in heating rate. Applying Doyle's approximation, Equation 3 can be reformulated as expressed by Flynn, Wall and Ozawa (Equation 4) [19, 20].

$$\log \beta = \text{Constant} - 0.4567 \frac{E_a}{RT} \quad (4)$$

The frequency factor (A) was also calculated using Equation 2. This analysis showed that the values derived by the Kissinger method were slightly lower than those obtained by the FWO method (Table 2).

Table 2. Kinetic parameters for ABAMPA decomposition obtained by the OFW and Kissinger methods

| Method | Activation energy [$\text{kJ}\cdot\text{mol}^{-1}$] | Frequency factor [s^{-1}] |
|-----------|---|--------------------------------------|
| Kissinger | 121.18 | 7.56×10^{11} |
| FWO | 123.31 | 1.27×10^{12} |

As shown in Table 2, the calculated activation energy and frequency factor for ABAMPA decomposition were determined by the Kissinger method to be 121.18 kJ/mol and $7.56 \times 10^{11} \text{ s}^{-1}$, respectively.

3.4 Half-life ($t_{1/2}$) determination

After determining the kinetic parameters (E_a and A) and assuming first-order reaction kinetics, the half-life can be calculated using the relation $t_{1/2} = 0.693/k$.

The rate constant (k) for the decomposition reaction is obtained from Equation 5 [21].

$$\log k = \log A - \frac{E_a}{2.3RT} \quad (5)$$

The $t_{1/2}$ values for ABAMPA decomposition were determined at four different temperatures using the derived activation energy and frequency factor, as summarized in Table 3. Figure 3 illustrates the temperature dependence of the $t_{1/2}$ for ABAMPA decomposition. In addition, the half-life of ABAMPA at 30 °C was calculated using both the Kissinger and the FOW methods. The Kissinger method predicted a half-life of approximately 22.05 years, whereas the FOW method yielded a value of around 30.52 years.

Table 3. The half-life of ABAMPA decomposition

| Temperature [°C] | Kissinger | | FWO | |
|---------------------|------------------------|-----------------|------------------------|-----------------|
| | k [s ⁻¹] | $t_{1/2}$ [min] | k [s ⁻¹] | $t_{1/2}$ [min] |
| 25 | 4.45×10^{-10} | 25967460.86 | 3.17×10^{-10} | 36441793 |
| 30 | 9.96×10^{-10} | 11594696.72 | 7.2×10^{-10} | 16042521.45 |
| 35 | 2.17×10^{-9} | 5314383.92 | 1.6×10^{-9} | 7252854.32 |
| 40 | 4.62×10^{-9} | 2497271.5 | 3.4×10^{-9} | 3363216.44 |

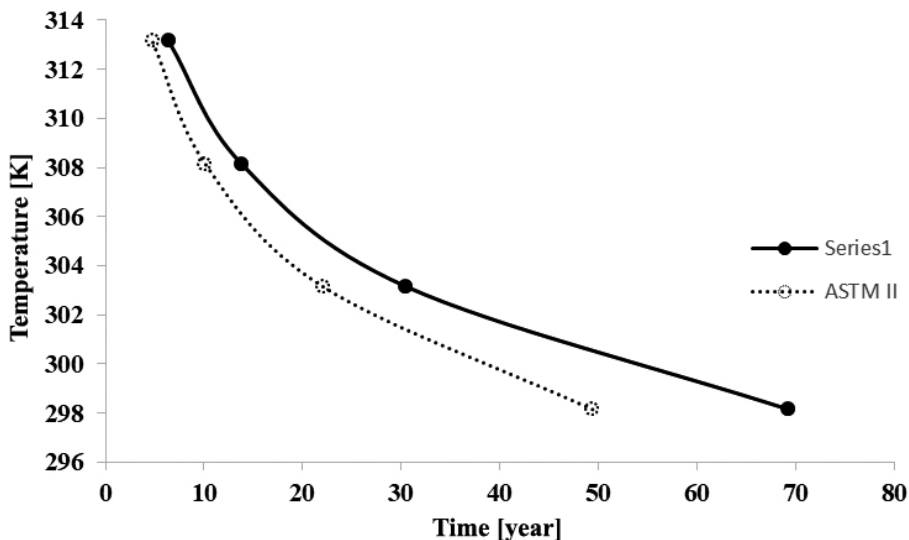


Figure 3. Dependence of half-life on temperature for ABAMPA decomposition

The exceptionally long half-life of ABAMPA decomposition (22.05-30.52 years at 30 °C by the Kissinger/FWO methods) demonstrates its remarkable thermal stability, which carries critical implications for its application in energetic formulations. The predicted decades-long persistence at ambient temperature (30 °C) suggests minimal degradation during storage, ensuring consistent performance in munitions and propellants over extended periods. Compared to conventional plasticizers, ABAMPA's stability could reduce maintenance costs and safety risks in storage management. The high activation energy barrier (implied by the long $t_{1/2}$) indicates resistance to accidental thermal initiation, making it preferable for applications requiring thermal robustness.

3.5 Critical explosion temperature (T_b)

T_b is a fundamental safety parameter for energetic materials including explosives, propellants, and pyrotechnics. It defines the minimum temperature at which a compound undergoes thermal runaway, initiating a self-sustaining exothermic process that may lead to uncontrolled explosion or combustion. Accurate determination of T_b is therefore essential for establishing safe handling protocols, storage conditions, transportation requirements, and disposal procedures for these materials.

The theoretical basis for T_b determination stems from combustion theory and incorporates key thermokinetic parameters, such as the activation energy, heat of reaction, and pre-exponential factor. For ABAMPA, the critical temperature was calculated using Equations 6 and 7 [22].

$$T_e = T_{e0} + \alpha\beta_i + b\beta_i^2 \quad (6)$$

$$T_b = \frac{E_a - \sqrt{E_a^2 - 4E_aRT_{e0}}}{2R} \quad (7)$$

In Equations 6 and 7, α and b represent coefficients, β is the heating rate, R is the universal gas constant, and E_a denotes the activation energy. The onset temperature, T_e , can be directly determined from the DSC curves at a given heating rate. As β approaches zero, T_e converges to its initial value, T_{e0} , as defined in Equation 6. Both the Kissinger and the FWO methods provide consistent predictions for the T_b value when applied through Equation 7. The calculated T_b values were 218.25 °C (FWO method) and 218.36 °C (Kissinger method), demonstrating excellent agreement between the two approaches.

3.6 Thermodynamic parameters

Following the determination of the kinetic parameters (activation energy and pre-exponential factor), the thermodynamic activation parameters for the decomposition reaction can be calculated using Equations 8-10 [23-25].

$$\Delta H^\ddagger = E_a - RT \quad (8)$$

$$\Delta G^\ddagger = E_a + RT_p \ln \left(\frac{K_B T_p}{h A} \right) \quad (9)$$

$$\Delta S^\ddagger = \frac{\Delta H^\ddagger - \Delta G^\ddagger}{T_p} \quad (10)$$

where ΔG^\ddagger is the Gibbs free energy of activation, ΔH^\ddagger is the enthalpy of activation and ΔS^\ddagger is the entropy of activation. In these calculations K_B represents the Boltzmann constant ($1.381 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$), h is Plank's constant ($6.626 \times 10^{-34} \text{ J S}$), and T_p corresponds to the DSC peak temperature (in K). The calculated thermodynamic parameters for ABAMPA decomposition are summarized in Table 4.

Table 4. Thermodynamics parameter values derived from the Kissinger and the FWO methods

| Method | $\Delta H^\ddagger (\text{kJ mol}^{-1})$ | $\Delta G^\ddagger (\text{kJ mol}^{-1})$ | $\Delta S^\ddagger (\text{J mol}^{-1})$ |
|-----------|--|--|---|
| Kissinger | 116.95 | 132.36 | -30.27 |
| FWO | 119.08 | 132.28 | -25.94 |

3.7 Comparison of ABAMPA with other selected azido ester energetic plasticizers

A comparison of the physicochemical properties of ABAMPA with DPGBAA, HETTAA, BAMP and DEGBAA is shown in Table 5. Their chemical structures are shown in Figure 4. The evaluated physicochemical properties include molecular formula, molecular weight (Mw), nitrogen content (N), oxygen balance (OB), T_g , and the heat of formation.

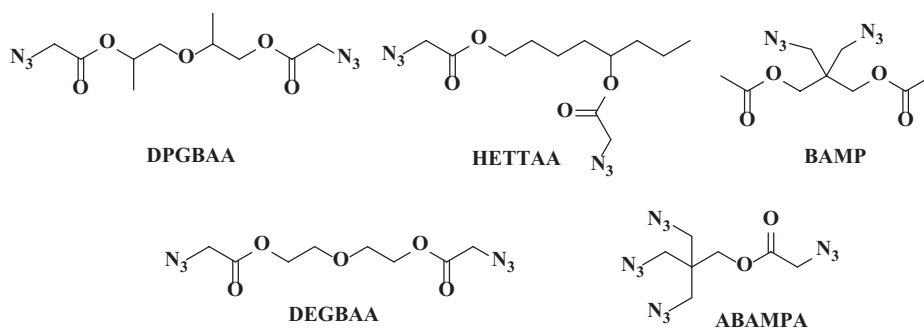


Figure 4. Chemical formulae of selected azido ester energetic plasticizers

Table 5. Physicochemical properties of ABAMPA and selected azido ester energetic plasticizers

| Parameter | DPGBAA | HETTAA | BAMP | DEGBAA | ABAMPA |
|---|---|---|--|--|---|
| Formula | C ₁₀ H ₁₆ N ₆ O ₅ | C ₁₂ H ₁₇ N ₉ O ₆ | C ₉ H ₁₄ N ₆ O ₄ | C ₈ H ₁₂ N ₆ O ₅ | C ₇ H ₁₀ N ₁₂ O ₂ |
| M _w [g·mol ⁻¹] | 300.28 | 383.33 | 270.249 | 272.221 | 294.23 |
| N [%] | 27.99 | 32.89 | 31.10 | 30.87 | 57.12 |
| OB [%] | -122.56 | -110.62 | -124.33 | -99.92 | -92.52 |
| T _g [°C] | -63.41 | -56.24 | -80.0 | -61.60 | -50.4 |
| ΔH _f [kJ·mol ⁻¹] | -403.56 | -259.59 | 242.0 | -302.91 | -1725.0 |
| ΔH _{dec.} [J·g ⁻¹] | 487.7 | 592.3 | — | 202.0 | 1750.89 |
| Ref. | [7] | [7] | [26] | [7] | [3] |

4 Conclusions

- ◆ ABAMPA exhibits significant potential as an effective energetic plasticizer for double-base propellant formulations.
- ◆ Comprehensive thermal characterization using DSC and TG analyses revealed its decomposition kinetics through two established non-isothermal methods: the Kissinger and the Flynn-Wall-Ozawa approaches. The calculated activation energies of 121.18 kJ mol⁻¹ (Kissinger) and 123.31 kJ mol⁻¹ (FWO) indicate good methodological consistency. Notably, ABAMPA exhibits remarkable thermal stability with a calculated half-life of 30.52 years at 30 °C. Moreover, key thermodynamic parameters governing ABAMPA's thermal decomposition behaviour were determined. These findings provide useful insights into ABAMPA's thermal properties, facilitating its optimized incorporation into propellant formulations.

- ◆ The consistent activation energy values obtained across four heating rates (5, 10, 15 and 20 K min⁻¹) validate the reliability of our kinetic analysis.
- ◆ The derived kinetic and thermodynamic parameters offer valuable guidance for tailoring ABAMPA containing propellant systems, particularly regarding their long term stability and performance characteristics.

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Declaration of competing interest

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Authorship contribution statement

Fatemeh Abrishami: conception, foundations, performing the experimental part

Erfan Yaghobi: foundations

Narges Zohari: performing the statistical analysis, other contribution to the publication

Atefeh Soufi: foundations, other contribution to the publication

Pourya Khakpour: performing statistical analysis

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