



## Thermochemical Evaluation of the Intrinsic Molecular Reactivity of Tosyl Azide and 4,4'-Diazidodiphenyl Ether and Sulfide

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**Abstract:** The exothermic decompositions of the tosyl azide **1** and two diazides, 4,4'-diazidodiphenyl ether,  $(\text{N}_3\text{C}_6\text{H}_4)_2\text{O}$  **2** and 4,4'-diazidodiphenyl sulfide,  $(\text{N}_3\text{C}_6\text{H}_4)_2\text{S}$  (**3**), were studied theoretically using the CHETAH protocol, and experimentally using DSC, weight loss TGA-FTIR and C80-FTIR techniques. Numerical modelling and MS-spectroscopy were also performed to estimate the nature of the intrinsic molecular reactivity of the azides **1–3** as possible early stages of an oxidative self-heating process.

**Keywords:** tosyl azide, aryl bisazides, thermal decomposition, mass spectra, TGA-FTIR, DSC, heat flux calorimetry, numerical modelling

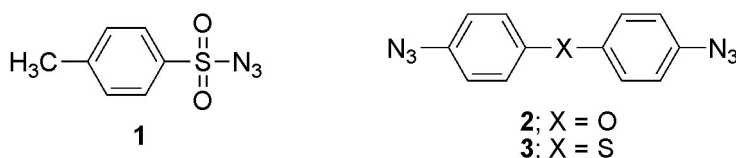
## Introduction

Organic azides are a vast and important class of compounds which, more than a century after their discovery, remain popular due to both their easy accessibility and incomparable synthetic utility [1, 2]. **The last two decades have seen overwhelming interest in these compounds due to the various simple routes by which they can be prepared and the ability to transform them into different substituents (amines, aza-ylides, isocyanates), reactive species (nitrene, nitrenium ion) and nitrogen-containing heterocycles (triazenes, triazoles, triazolines, azirines, aziridines).**

Although the toxic and explosive properties of some metal azides and a few organic azides, [3-5] **including tosyl azide, [6]** are well documented, less attention has been paid to the healthy and safe disposal of this class of compounds. In addition, the chemical properties of a series of nitrogen rich covalent azides, and their potential use as high energy-density materials (HEDM), are presently under investigation [7]. **The azido group is a highly energetic functional group that adds 293 kJ mol<sup>-1</sup> to the energy content of a molecule [8].**

The hazardous properties of these oxygen-less compounds are attributed to the easy polarization of the  $-N_3$   $\pi$ -bond, which facilitates  $N_2$  extrusion [9]. Many organic compounds containing one or more azido groups, when subjected to thermal or mechanical shock, [3] undergo dissociation of their azido group(s) into a nitrene and molecular nitrogen, a process that is accompanied by the release of large amounts of energy. In the presence of a high boiling solvent (i.e., controlled conditions) or a large substrate, this energy is dissipated and the nitrene produced by the reaction, in the singlet or triplet state, is of great synthetic utility [2]. As a result, interest in these potentially explosive molecules has steadily grown as researchers have overcome their awe of the hazard posed by handling them [10, 11].

In the present study, we measured various thermodynamic variables of the tosyl azide **1**, 4,4'-diazidophenyl ether **2**, and the 4,4'-diazidophenyl sulfide **3** (Scheme 1). **These compounds were selected as significant examples of a series of nitrogen rich covalent azides whose dangerous threshold values, given by the molecular composition ratio (C+O+S)/N, are  $\leq 3$ .**



**Scheme 1.** Structures of the azides **1–3**.

This was achieved using calorimetric methods (DSC, TG-FTIR and the Heat-Flux SETARAM C80 calorimeter coupled with FTIR analyser) under both oxidative and non-oxidative conditions, together with theoretical calculations using the CHETAH software. In addition, numerical modelling and mass spectroscopy (EI, 70 eV) were performed in order to determine the possible early-stages of the thermal decomposition of the azides **1–3**.

## Theory

In spite of the fact that organic azides are generally stable toward common oxidants and acidic aqueous solutions, azides with large positive heats of formation ( $\Delta_f H$ ) are inherently unstable. The reasons underlying a molecule's reactivity or lack of stability can be elucidated by examining thermodynamic parameters, and also by scrutinizing kinetic variables, critical temperatures, [12] numerical protocol based on the symmetries and geometries, spatial distributions and energies of a few dominant orbitals, and electric polarizabilities and hyperpolarizabilities. Therefore, important information could be provided by:

- i) Enthalpies of reaction ( $\Delta H^\ddagger$ ), calculated from heats of formation [ $\Delta_r H = \sum_{\text{products}} \Delta_f H - \sum_{\text{reactant}} \Delta_f H$ ] at 298 K, and Gibbs free energies of reaction ( $\Delta G^\ddagger$ ) [ $\Delta_r G = \Delta_r H - T\Delta S$ ].
- ii) Arrhenius activation energies ( $E_a$ ), calculated from the rate of reaction ( $\ln k$ ) and the *frequency factor*, from which the enthalpies [ $E_a = \Delta H^\ddagger + RT$ ] and entropies ( $\Delta S_a$ ) of activation can be calculated.
- iii) HOMO-LUMO energies and orbital symmetry. Fast reactivity may be due to a small LUMO-HOMO energy difference [13].
- iv) The polarization of the  $-\text{N}_3$   $\pi$ -bond and  $-\text{N}-\text{N}_2$  bond energy and length. A higher electric polarizability enhances the instability/reactivity.
- v) Ionization energy. In the general case, represents the energy required to detach one electron from a neutral molecule (or atom). Qualitative information on the ionization energy for a selected class of molecules can be obtained using electron impact (EI) mass spectroscopy.

Thermodynamic variables (heats of formation  $\Delta_f H$ , combustion  $\Delta_c H$ , and decomposition  $\Delta_d H$ ) and molecular nitrogen loss (%) can be predicted using the CHETAH (CHEMical Thermodynamic and Hazard Evaluation) software. The data calculated using CHETAH for the azides **1-3** are listed in Table 1.

**Table 1.** CHETAH calculated energetic parameters ( $\Delta_f H$ ,  $\Delta_c H$ ,  $\Delta_d H$ ) and %  $N_2$  loss for the azides **1-3**

	1	2	3
$\Delta_f H$ (kJ g <sup>-1</sup> )	1.61	2.61	3.12
$\Delta_c H$ (kJ g <sup>-1</sup> )	-21.37	-25.16	-25.43
$\Delta_d H$ (max J g <sup>-1</sup> )	-4497	-4010	-3677
$N_2$ (%)	21.29	33.3	31.3

## Experiments

The three sensitive organic azides used in this study (see Scheme 1) were prepared as follows. The tosyl azide **1** was prepared according to a previously described protocol [14], and the bisazides **2** and **3** were prepared according to the Dutt-Wormall reaction by diazotization of the corresponding amines and treatment with the azido ion of the resulting diazonium salts [15, 16]. The <sup>1</sup>H-, <sup>13</sup>C-NMR and IR spectra of each compound were in agreement with those reported in the literature [14-16]. The melting points of the solid azides **2** and **3**, taken from the endothermic melting peak in the DSC thermogram, were 74 °C and 86 °C, respectively, in agreement with the previously reported values [15, 16].

The heats of the decomposition ( $\Delta_d H$ ) for the azides **1-3** are all predicted to be over the threshold of -2930 J g<sup>-1</sup> above which these compounds are considered dangerous (Table 1) [17, 18]. Moreover, comparison of the CHETAH-predicted heats of formation ( $\Delta_f H$ ) with those obtained using the less computationally intensive Thermochemical recipes code T1 at 298 K in gas phase [19] revealed that for azides **2** and **3**, the values obtained using the two approaches differed by less than 5% (658.2 vs 692.1 kJ mol<sup>-1</sup> and 837.1 vs 860.4 kJ mol<sup>-1</sup>, respectively), while for azide **1**, the difference was much greater (317.2 vs 114.2 kJ mol<sup>-1</sup>).

The data predicted using the CHETAH software are merely indicative even if very useful, [20] more realistic results can be obtained by experimental DSC, TG-DTA and SETARAM C80-FTIR calorimetry. These techniques enable us to characterize the thermal (in)stability of the azides **1-3** via the determination of some physical (pressures  $P$ , temperatures  $T_n$  and decomposition rates) and energetic (activation energy  $E_a$ , enthalpies and entropies of decomposition) parameters.

**Table 2.** DSC heats of decomposition ( $\Delta_d H$ , J g<sup>-1</sup>) and temperatures (°C) of the thermal decomposition (TD) of the azides **1-3**<sup>a</sup>

	$\Delta_d H_{\text{air}}^b$	$\Delta_d H^c$	$\Delta_d H_{\text{SCC}}^d$	$T_0^e$	$T_{\text{EOT}}^f$	$T_p^g$	$T_{\text{EET}}^h$
<b>1</b>	-1806	-1640	-1583	121	156	184	204
<b>2</b>	-2045	-1562	-1715	124	154	177	192
<b>3</b>	-1340	-1303	-1369	128	167	190	207

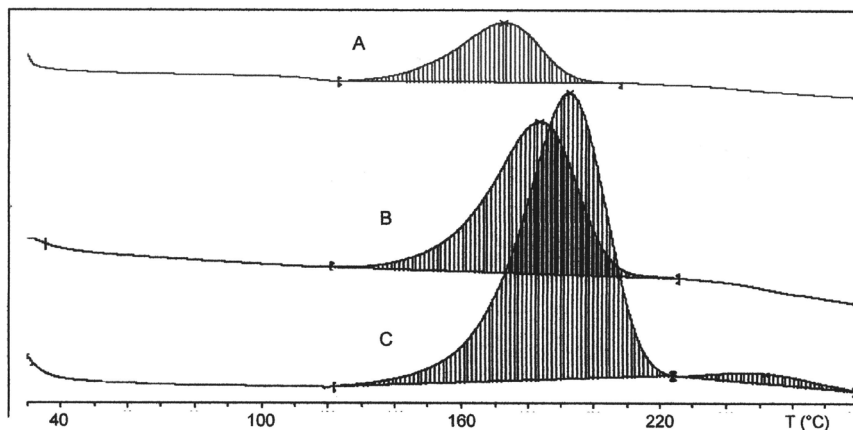
<sup>a</sup> TD data refer to a scan rate ( $\phi$ ) of 5 °C min<sup>-1</sup>;

<sup>b</sup> in static air; <sup>c</sup> under nitrogen;

<sup>d</sup> in a closed steel vessel;

<sup>e-f</sup> respectively initial, exothermic onset, peak and exothermic endset temperature.

The data reported in Table 2 account for TD involving compounds with different sensitivities under oxidative heating. The heat capacities of azides **2** and **3** measured using the closed-vessel were larger than those measured using an open-vessel; following Le Chatelier's principle, this difference can be attributed to the exothermic decomposition of the azides being accompanied by greater gas evolution in the latter cell type. By contrast, azide **1** exhibited the opposite behavior.



**Figure 1.** Individual TD DSC curves for DSC runs performed under nitrogen at scanning rates ( $\phi$ ) of 2.0, 5.0 and 10.0 °C min<sup>-1</sup> with 2.4, 2.4 and 3.8 mg, curves A, B and C respectively, of azide **1**.

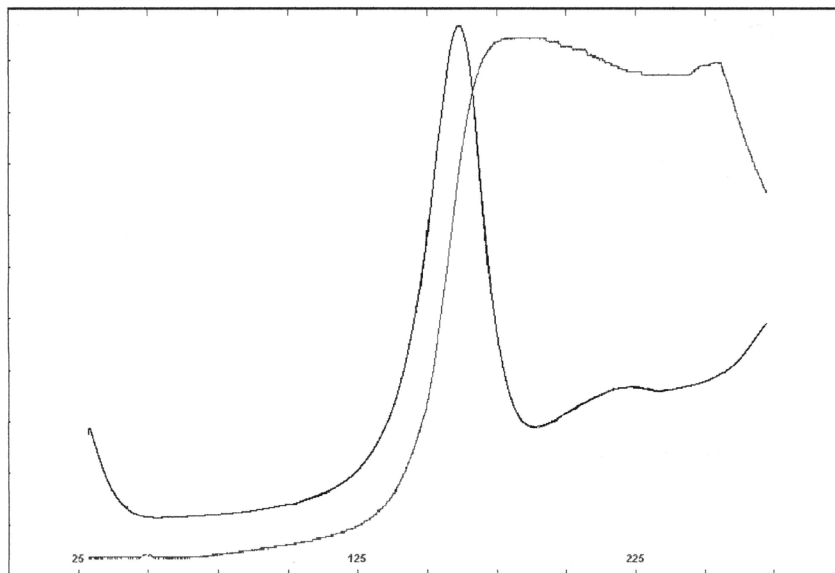
The DSC curves, (Figure 1) measured at different heating rates in the range 30.0-280.0 °C, were analyzed using the ASTM E698 method for reactions whose behavior is well described by the Arrhenius equation. From a plot of log

$b$  (where  $b$  = heating rate in  $\text{K min}^{-1}$ ) against  $1/T$  ( $T$  = peak temperature in K), the activation energies ( $E_a$ ), pre-exponential factor  $A^0$  and kinetic constant  $k$  for each absolute temperature can be calculated.

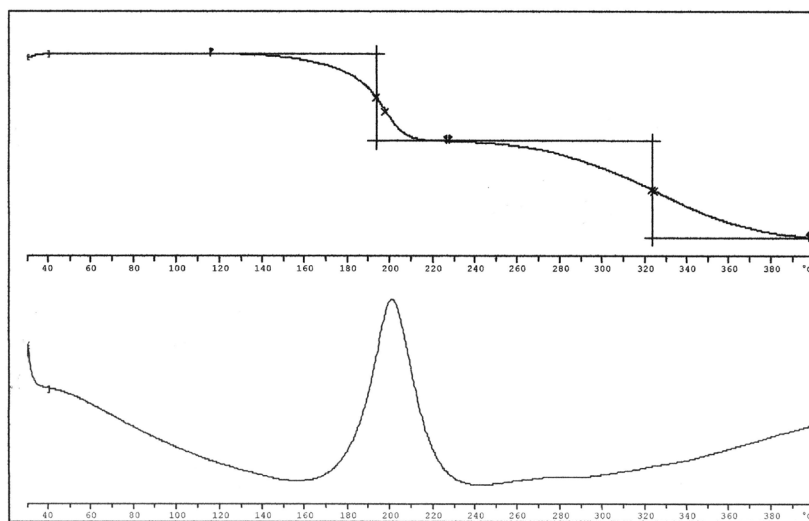
The TD reactions of the oily azide **1** (m.p. 24-26 °C) and the solid azides **2** and **3** were each treated as having first-order kinetics as plots of  $\ln(k/\text{min}^{-1})$  vs  $T/\text{K}$  showed a linear trend with correlation coefficients in the range of 0.999-1. The activation energies ( $E_a$ ) of **1**, **2**, and **3** were calculated to be 127.5, 138.6 and 137.7  $\text{kJ mol}^{-1}$ , respectively, with corresponding  $\ln A^0/\text{min}^{-1}$  values of 28.5, 31.1 and 30.6. Assuming unimolecular processes, we calculated the activation enthalpies ( $\Delta H^\ddagger$ ) and entropies ( $\Delta S$ ) from the data. The  $\Delta H^\ddagger$  values obtained were 125.1  $\text{kJ mol}^{-1}$  for **1** (146.8  $\text{kJ mol}^{-1}$  in Ref. [19]), 136.2  $\text{kJ mol}^{-1}$  for **2**, and 135.3  $\text{kJ mol}^{-1}$  for **3**, and the  $\Delta S$  value for **1** was 9.9  $\text{J K}^{-1} \text{mol}^{-1}$ , 35.2  $\text{J K}^{-1} \text{mol}^{-1}$  for **2**, and 34.9  $\text{J K}^{-1} \text{mol}^{-1}$  for **3**. No thermal data are available in the literature for the azides **2** and **3**, while 'controlled' thermal decomposition of **1** has been carried out in various solvents, starting from the pioneering works of Breslow [21].

By TG-FTIR and C80-FTIR analyses of the azides **1-3**, more accurate data for the weight loss, temperatures  $T_n$ , and heats of decomposition were obtained, along with information on the pressure change associated with the TD process in a closed-vessel. For **1**, the C80-FTIR analysis (see Figure 2) detected at least two exothermic processes, at  $T_i = 103$  and  $190$  °C with  $\Delta_a H$  -1487  $\text{J g}^{-1}$  and -52  $\text{J g}^{-1}$  respectively, and a pressure increment ( $\Delta P$ ) of 5 bar. The TG analysis (see Figure 3) showed that these two processes have corresponding weight losses of 28.6% and 31.4%, which are respectively higher and lower than the corresponding loss of  $\text{N}_2$  and  $\text{SO}_2$ .

The C80 and TG thermal analyses coupled with FTIR spectroscopy allowed the identification of the molecular fragments and gases produced by the TDs of the azides. The thus identified fragments and gases for **1** were carbon dioxide ( $\text{CO}_2$ ), carbon monoxide (CO), sulfur dioxide ( $\text{SO}_2$ ), thioxomethanone (COS), sulfur dioxide ( $\text{SO}_2$ ), ammonia ( $\text{NH}_3$ ) and toluene ( $\text{C}_7\text{H}_8$ ).

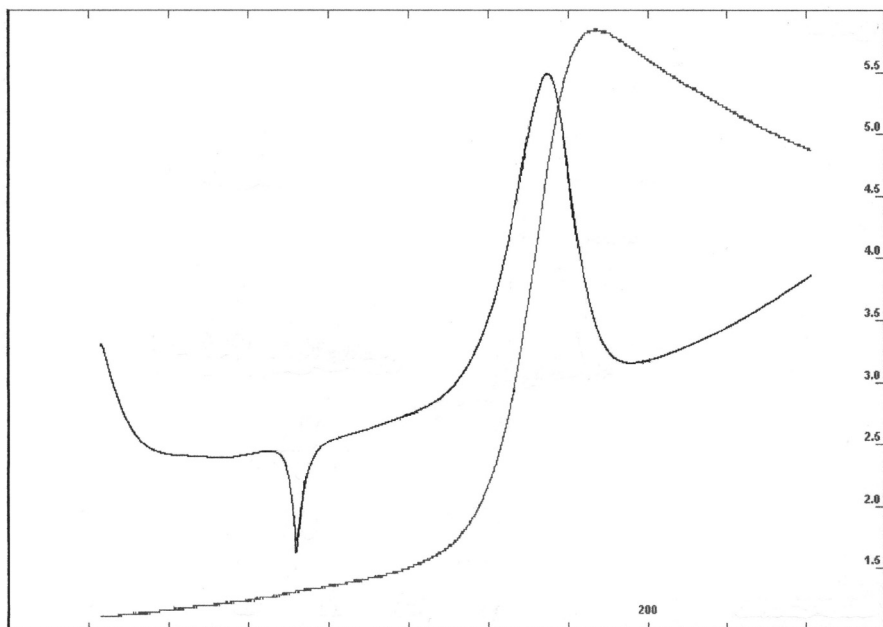


**Figure 2.** C80 curve for azide 1 recorded in the temperature range 30.0-280.0 °C at a scan rate ( $\phi$ ) of 0.5 °C min<sup>-1</sup>.



**Figure 3.** TG (upper) and DTA (Differential Thermal Analysis) (lower) curves of azide 1 recorded in the temperature range 30.0-400.0 °C with a scan rate of  $\phi = 20$  °C min<sup>-1</sup> under an 80 mL min<sup>-1</sup> N<sub>2</sub> flow.

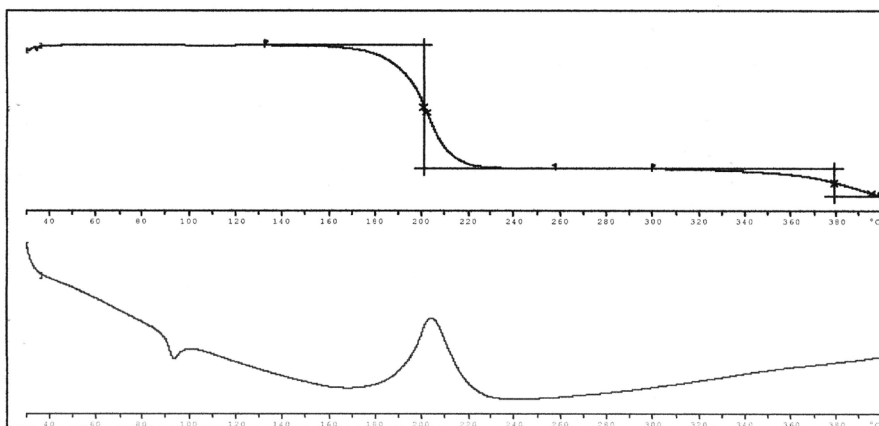
On the other hand, the C80 analyses of azides **2** and **3** showed in both cases an endothermic melting peak and an exothermic decomposition starting at  $T_i = 120$ - $125$  °C, with  $\Delta_d H$   $-1487$  J g $^{-1}$  and  $-1526$  J g $^{-1}$  and pressure increments of  $\Delta P = 5$  and  $4$  bar, respectively. As an example, the C80 curve for azide **3** is shown in Figure 4.



**Figure 4.** C80 curve of the azide **3** performed in the temperature range  $30.0$ - $280.0$  °C with a scan rate of  $\phi = 0.5$  °C min.

TG analysis showed that the TD processes for **2** and **3** correspond to weight losses of  $24.6\%$  and  $22.4\%$ , which are close to the respective loss of two moles of  $N_2$  (see Figure 5 for **3**).





**Figure 5.** TG curve (upper) and SDTA curve (lower) of the azide **3** performed over the temperature range 30.0-400.0 °C with a scan rate of  $\phi = 20$  °C  $\text{min}^{-1}$  under an 80 mL  $\text{min}^{-1}$   $\text{N}_2$  flow.

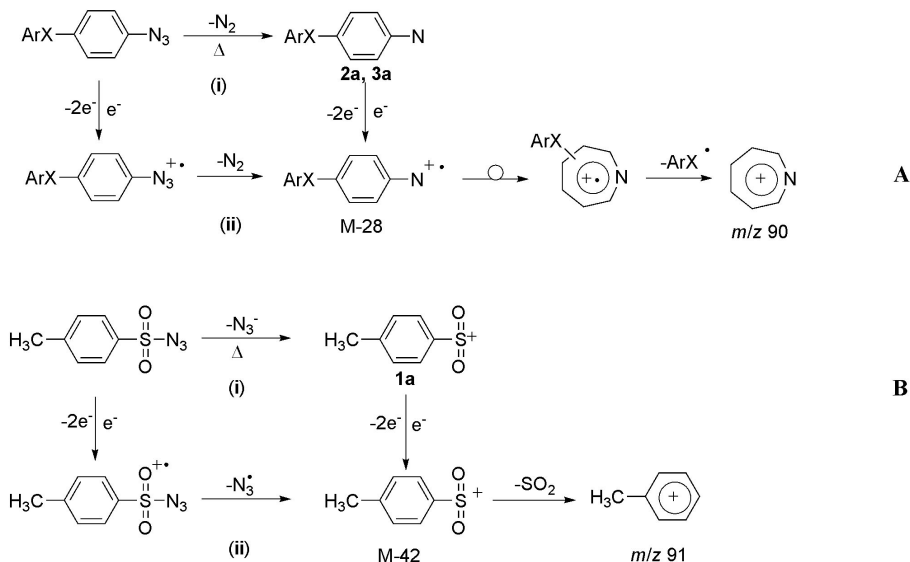
Numerical modelling and mass spectra analyses can be used to suggest the possible initial steps of the unimolecular TD of the azides **1-3**. The following main fragmentations were obtained by EI-MS (70 eV,  $m/z$ ):

- 1, 197( $\text{M}^+$ , 5.7%), 155(M-42, 62.4), 91\*, 65 (23.4);
- 2, 252( $\text{M}^+$ , 11.6%), 224(M-28, 37.1), 196(M-56, 9.8), 90\*, 63 (22.1);
- 3, 268( $\text{M}^+$ , 22.6%), 240(M-28, 48.5), 212(M-56, 29.2), 90\*, 63 (23.9);

where values in parentheses correspond to the relative intensity and the asterisk denotes the base peak (100%).

The peaks of the molecular ions ( $\text{M}^+$ ) represent the ionized molecules. As expected, the primary fragmentations of the azides **2** and **3** involve the loss of neutral  $\text{N}_2$  to generate the odd-electron species  $\text{ArN}^{+\cdot}$  (M-28) (see Scheme 2 A). Conversely, the azide **1** loses the  $\text{N}_3$  radical, presumably from the molecular ion  $\text{M}^+$ , or the  $\cdot\text{N}_3$  anion directly [22] (see Scheme 2 B). The behavior of **2** and **3** can be adequately described by the *normal* fragmentation pattern of aryl azides, [23] in which the critical energy for  $\text{ArN}_3^{+\cdot} \rightarrow \text{ArN}^{+\cdot} + \text{N}_2$  is equivalent to the dissociation energy of the  $\text{ArN-N}_2$  bond plus the ionization energy ( $I$ ) of the radical  $\text{ArN}^{\cdot}$ , because the reverse process is insignificant. The ionization energy generally requires twice the energy required for bond dissociation (bond lability). On the other hand, the *abnormal* azido fragmentation pattern observed for **1** can be interpreted by assuming that under the ion chamber conditions used ( $T = 220$  °C and  $P = 10^{-2}$  Pa), the reaction  $\text{ToSO}_2\text{-N}_3 \rightarrow \text{ToSO}_2^+ + \cdot\text{N}_3$  is favored with respect to the ionization process to  $\text{ToSO}_2\text{-N}_3^{+\cdot}$  and other possible

pathways such as  $\text{ToSO}_2\text{-N}_3^{+\bullet} \rightarrow \text{ToSO}_2\text{-N}^{+\bullet} + \text{N}_2$  or  $\text{ToSO}_2\text{-N}_3 \rightarrow \text{ToSO}_2\text{-N}(\text{S or T}) + \text{N}_2$  [24].



**Scheme 2.** Main fragmentation patterns for the azides **1** (**B**) and **2** and **3** (**A**) determined by EI-mass spectrometry (70 eV).

On the basis of the present data and previous reports on **1**, we can argue that the TD of this azide occurs via a number of concomitant heterolytic and homolytic bond cleavage pathways [20].

## Computational results

Using density functional theory (DFT) at the B3LYP/6-31G\* level, we calculated the ground state energies (including the LUMO-HOMO separations) of the initial states and the possible transient intermediates and structures connecting them at HF/6-31G\* including zero-point vibrational energy. In addition, we calculated the enthalpies of reaction by numerical modelling based on Thermochemical recipes T1 for the heats of formation ( $\Delta_f H$ ), which required previous calculations at the HF/6-31G\* level [19]. The results of these calculations are listed in Table 3.

**Table 3.** Energies ( $\Delta E$ ) of the N-N<sub>2</sub> bond dissociation of **1-3** calculated using DFT method at B3LYP/6-31G\*//HF6-31G\* level relative to the azides in the ground state and the nitrenes **1a-3a** (as singlet states S<sub>0</sub>) intermediates for the path (i) in Scheme 2 (A); FMO energies and the LUMO-HOMO separation

	$\Delta E^a$	$E_{\text{HOMO}}$	$E_{\text{LUMO}}$	$\Delta E^b$
<b>1</b>	124.4	-938.9	220.6	1159.7
<b>2</b>	152.8	-559.6	-109.3	450.3
<b>3</b>	155.7	-553.5	-126.8	426.7

<sup>a</sup> Calculated energies of bond dissociation in kJ mol<sup>-1</sup> performed by B3LYP/6-31G\* including ZPE correction.

<sup>b</sup> LUMO-HOMO differences in kJ mol<sup>-1</sup>.

For most classes of compounds, the primary cleavage (thermal impact sensitivity) is a qualitative indicator of the stability of a compound, and thus can be used to compare the stabilities of compounds subjected to thermal processes under the same conditions. The energies obtained at the (U)B3LYP level of theory for the reaction  $\text{ToSO}_2\text{-N}_3 \rightarrow \text{ToSO}_2\text{-N}_{(\text{S or T})} + \text{N}_2$  predict that the separation between the lowest triplet state and the ground state singlet is 49.5 kJ mol<sup>-1</sup>. The calculations of the corresponding enthalpies of reaction involving the  $\text{ToSO}_2\text{-N}_{(\text{S})}$  in the singlet state 124.4 kJ mol<sup>-1</sup> and triplet state ( $\text{ToSO}_2\text{-N}_{(\text{T})}$ ) 74.8 kJ mol<sup>-1</sup> confirmed the expectation that the loss of N<sub>2</sub> would be the most favored thermal process for **1** [21]. From the data in Table 3, the azide **1** appears to be more stable than the bisazides **2** and **3** from both the thermodynamic and HOMO-LUMO energetic viewpoints. The (U)B3LYP calculations for these latter azides **2** and **3** give low energetic singlet ground states favoured over the respective triplet ground states according to reported data [16]. The ionization pathways on the potential surface of the azide **1** are mainly localized on the SO<sub>2</sub> group, which induces weak polarization of the -N<sub>3</sub> π-bond to -N-N<sub>2</sub>. Conversely, an ionization pathway localized on the azido group of the azides **2** and **3** enhances the lack of stability, or reactivity, of these compounds.

## Conclusion

We have assessed the thermal decomposition behavior of three organic azides using calorimetric analyses and quantitative structure-property relationships based on molecular modelling. In addition, we focused on predicting the impact sensitivity via examination of electronic structure correlations, in order to

estimate the nature of the intrinsic molecular reactivity of the azide **1** and the bisazides **2** and **3** as possible early stages of an oxidative self-heating process. The correlations revealed in this work provide a better understanding of the impact sensitivity from a molecular viewpoint, which should assist in classifying highly energetic materials.

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