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ORIGINAL RESEARCH

Theoretical studies on stability and pyrolysis mechanism of salts formed by N_5^- and metallic cations Na^+, Fe^{2+} and Ni^{2+}

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Abstract The salts formed by N_5^- and metallic cations (Na^+, Fe^{2+} and Ni^{2+}) may be potential candidates for superior energetic materials and were studied with the density functional theory B3LYP method and ab initio molecular orbital theory MP2 method using the 6-31G* and LanL2DZ basis sets. Thermal dissociations of these salts are initiated by breaking of the N_5 ring, and those of $Fe(N_5)_2$ and $Ni(N_5)_2$ proceed sequentially through two transition states. In gas phase, the activation barriers (E_as, in kJ/mol) of thermal dissociations decrease in the order of $N_5^- > NaN_5 > HN_5 > Ni(N_5)_2 > Fe(N_5)_2$. Products of initial pyrolysis of these salts are N_2 and metallic azide. The frontier orbital energy gaps (in eV) are N_5^- (8.27) > HN_5 (7.40) > NaN_5 (5.10) > $Fe(N_5)_2$ (4.92) > $Ni(N_5)_2$ (3.43). The more stable salt has the smaller electron transfer between the cation and anion.

Keywords N_5^- salts · Stability · Initial pyrolysis · First principle methods

Introduction

High nitrogen compounds are of significant interest as potential candidates for superior energetic materials [1–5]. For these compounds, large number of N–N and N=N bonds will convert into N≡N (N_2) on explosion, and bond dissociation energies (BDEs) of the former (163.2 and 418.4 kcal/mol, respectively) are much lower than that of the latter (954.0 kcal/mol) [6], therefore, a large amount of heats will be released.

Many theoretical studies showed that some all-nitrogen compounds (N_n, such as N_4, N_6, N_7, N_8 N_9 and N_{10}) might be vibrationally stable and could be valuable targets for synthesis [2–4, 7–10]. However, up to now, N_4 is the only experimentally observed metastable N_n species with a lifetime exceeding 1 μs [11]. In addition, the non-neutral species such as N_3^+ and N_4^+ only exist in gas phase [12]. Compared with the other N_n compounds, the studies on the derivatives of N_3^- are more fruitful [13–21]. Schleyer et al. [22, 23] and Nguyen and Ha [5] have illustrated theoretically that the most stable all-nitrogen systems, after N_2, are pentazolic units and that HN_5 and N_5^- should be comparable in aromaticity to furan and pyrrole. In 1992, Bartlett's group [24] predicted the activation barrier (19.8 kcal/mol) for the decomposition of HN_5 and showed that HN_5 and N_5^- should be viable existent under appropriate conditions. Ostmark et al. [25] and Vij et al. [26] have detected N_5^- in gas phase from high-energy mass spectrometric degradation of aryl pentazoles. The acidity of HN_5 has been estimated to be stronger than that of HNO_3 [27]. Hence, if HN_5 is generated in the aqueous solution of nitrate, N_5^- will be produced and metallic salts can be formed [28]. Theoretical studies [29–34] suggested that the metallic salts of N_5^- should be stable. $Fe(N_5)_2$ which is isoelectronic with $Fe(CO)_5$ and $Fe(C_5H_5)_2$ was predicted to be a tightly bonded complex and its total metal–ligand bond energy (456.1 kJ/mol) is only 121.3 kJ/mol less than that of ferrocene (577.4 kJ/mol) [29]. It has higher metal–ligand bond energy and stronger metal–ligand interactions than the isomer $Fe(N_2)_5$, so it may be a possible candidate for high-energy compounds [29]. The divalent cation of Ni, the element neighbouring Fe in the periodic table, can coordinate with N_5^- too to form $Ni(N_5)_2$ which may be also a potential candidate of high-energy compounds.

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In this paper, two kinds of N_5^- complexes $M(N_5)_2$ (M = Fe and Ni) and MN_5 (M = Na) were studied. To assess their thermal and chemical stabilities, the initial pyrolysis processes and the electron transfer between the cation and anion were predicted.

Computational details

Geometry optimizations of the molecular structures and transition states (TSs) were carried out at the B3LYP/6-31G* level and the B3LYP/gen level with the 6-31G* basis set for N and Lanl2dz for metal which are widely used for calculations of TSs [35–39] with the Gaussian program package [40]. The optimized structures were confirmed to be local minima without imaginary frequencies and the optimized TSs were confirmed by only one imaginary frequency. Single point energies of molecular structures obtained at the B3LYP/6-31G* and B3LYP/gen levels were evaluated at the MP2/6-31G* and MP2/gen levels, respectively. The relaxed potential energy surfaces along with the stretching of N–N bonds were scanned for locating TSs at the B3LYP/6-31G* level. The natural bond orbital (NBO) analyses were performed [41] to analyze the atomic charge distributions at the B3LYP/6-31G* level. It is worth noting that charges are not physically observed and may be questionable to deal with atoms from different rows.

Changes in enthalpy and free energy (ΔHs and ΔGs) of the formation reactions and decomposition reactions at 298.15 K were obtained by Eqs. (1) and (2):

$$\Delta H = \sum H_P - \sum H_R, \tag{1}$$

$$\Delta G = \sum G_P - \sum G_R. \tag{2}$$

$\sum H_P$ and $\sum H_R$ represent the sums of enthalpies of products and reactants in the formation reactions and decomposition reactions, respectively. $\sum G_P$ and $\sum G_R$ are the corresponding items of free energies.

The activation energy barrier (E_a) was calculated using the Eq. (3)

$$E_a = E_{TS} - E_R. \tag{3}$$

E_{TS} and E_R represent the total energies of the transition state and reactant, respectively. Calculations of the activation enthalpy and activation free energy ($\Delta H^{\neq}$ and $\Delta G^{\neq}$) were similar to that of E_a.

The enthalpy of sublimation (ΔH_{sub}) was estimated using the Eq. (4) suggested by Rice and Polizer et al. [42, 43]:

$$\Delta H_{sub} = \alpha(A_s)^2 + \beta(\nu\sigma^2_{tot})^{0.5} + \gamma, \tag{4}$$

where A_s is the surface area of the 0.001e/borh^3 isosurface of the electron density, σ^2_{tot} is the total variances of the surface electrostatic potential and ν indicates the degree of balance between the positive and negative electrostatic potentials. These indexes were obtained at the B3LYP/6-31G* level using the Multiwfn program [44]. The values of coefficients α, β and γ were taken from Ref. [42]. It is worth noting that ΔH_{sub}s of title salts were estimated roughly because the used method was proposed based on the compounds with C, H, O and N atoms only.

Results and discussion

Structure

Conformations of salts formed by the pentazole anion (N_5^-) and metallic cations are mutable, the most stable structures are different according to the different metal counter ions. Burke et al. [30] studied different conformations of several salts formed by N_5^- and metallic cations (K^+, Mg^{2+}, Ca^{2+} and Zn^{2+}) at different levels. They proposed that structure I shown in Fig. 1 was most energetically favoured for most salts and the structure II was also favourable in some cases. So structures I and II of title salts (NaN_5, $Fe(N_5)_2$ and $Ni(N_5)_2$) were built as the original structures for optimization. The single point energies of conformations I and II obtained at the MP2/6-31G*//B3LYP/6-31G* and MP2/gen//B3LYP/gen levels are listed in Table 1. The energy differences between I and II ($\Delta E = E_{II} - E_I$) suggest that the most energetically favoured structures are I for NaN_5 and $Ni(N_5)_2$. For $Fe(N_5)_2$, the most stable conformation is not the same at different levels. Lein et al. have studied various conformations of $Fe(N_5)_2$ at three levels and found that II is most stable [29]. Therefore, the conformation II of $Fe(N_5)_2$ was studied in this paper. Figure 2 shows the energetically favoured structures with the atomic charge distributions. For comparison, the optimized structures of N_5^- and HN_5 are also presented. In the following studies, we focus on these energetically favoured structures only.

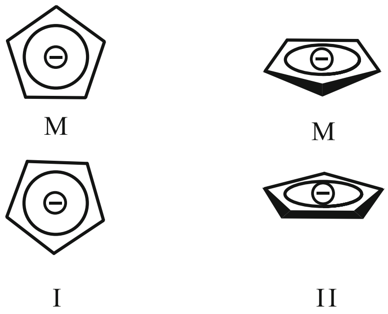
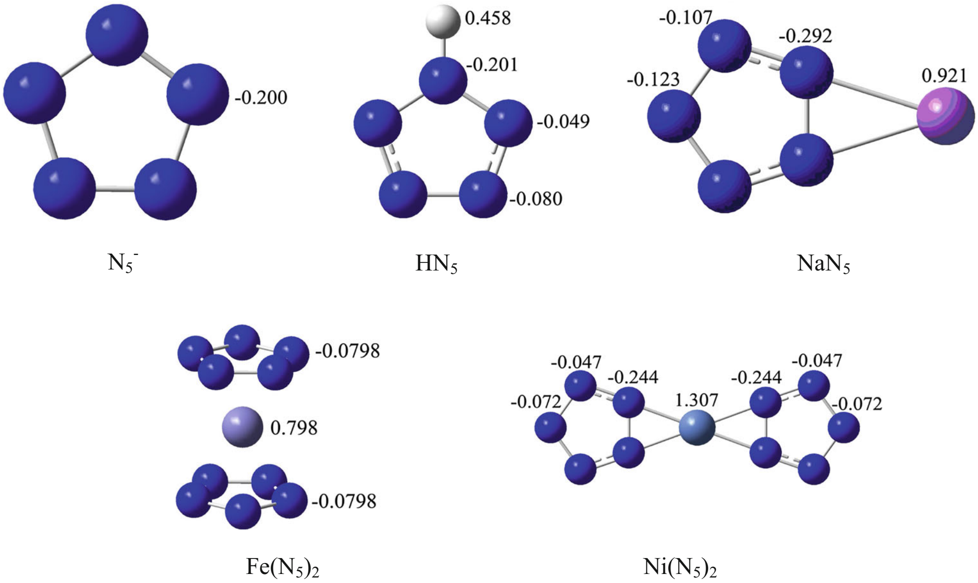


Fig. 1 Original structures (M = Na^+, Fe^{2+}, and Ni^{2+}; for M = Na^+, only one N_5^- ring appears)

Table 1 Predicted single point energies (E) of different conformations at the MP2/6-31G*//B3LYP/6-31G* and MP2/gen//B3LYP/gen levels

	Energy	NaN_5	$Fe(N_5)_2$	$Ni(N_5)_2$
MP2/6-31G*	E_I (a.u.)	−434.87634	−1808.25326	−2052.75277
	E_{II} (a.u.)	−434.87080	−1808.26221	−2052.74605
	ΔE (a.u.)	0.00554	−0.00896	0.00672
MP2/gen	E_I (a.u.)	−273.19830	−668.54664	−714.28487
	E_{II} (a.u.)	−273.18988	−668.51232	−714.25288
	ΔE (a.u.)	0.008418	0.034318	0.031996



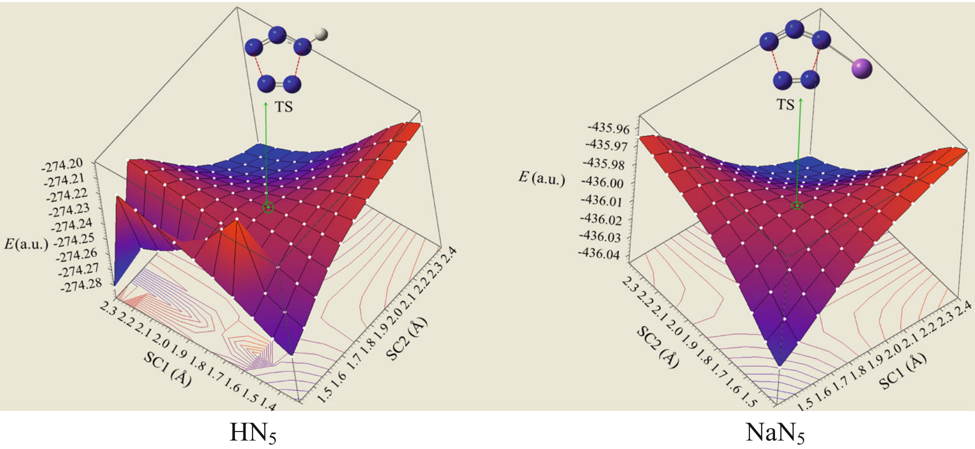
N_5^- HN_5 NaN_5

$Fe(N_5)_2$ $Ni(N_5)_2$

Fig. 2 Most energetically favoured structures and atomic charge (in e) distributions

Thermal stability and initial pyrolysis process

Thermal stability plays an important role in evaluating the synthetic possibilities and practical applications of energetic materials, which can be reflected by the activation energy (E_a) of thermal dissociation. Since the transition state (TS) determines E_a, the pyrolysis mechanism, and the final products, it is of primary importance to find TS. Previous studies reported that molecules with the N_5 ring usually decompose into N_2 and azido compounds [25, 28, 45]. Therefore, the potential energy surface with respect to two N–N bonds (SC1 and SC2) of the N_5 ring was simulated. For comparison, the corresponding surface of HN_5 was also studied. Figure 3 shows the results of NaN_5 and HN_5. Obviously, NaN_5 and HN_5 have similar TSs, and the final products are N_2 and XN_3 (X = Na or H). So we infer



HN_5 NaN_5

Fig. 3 Potential energy surfaces with respect to two N–N bonds at the B3LYP/6-31G* level that the initial pyrolysis of the salts formed by N_5^- and metallic ions may be similar to that of HN_5, i.e. the process proceeds through a TS of $MN_3 \cdots N_2$ or $M(N_5)N_3 \cdots N_2$ type with the distances of two broken N–N bonds around 1.7 Å and the initial products are N_2 and MN_3 or $M(N_5)N_3$.

The pyrolysis processes with the structures of TSs and products, and the E_as of the processes and reverse processes are shown in Fig. 4. The pyrolysis processes of N_5^-, HN_5 and NaN_5 go through one TS, while that of $Fe(N_5)_2$ and $Ni(N_5)_2$ have two TSs, which is because the latter has one more N_5 ring than the former and two rings break sequentially, not simultaneously. The pyrolysis reactions and the corresponding activation enthalpies ($\Delta H^{\neq}$s), activation free energies ($\Delta G^{\neq}$s) and the changes in thermodynamic properties (ΔHs and ΔGs) are tabulated in Table 2. $\Delta H^{\neq}$s and $\Delta G^{\neq}$s of all reactions are positive, so activation processes require excess energy and are not spontaneous. ΔHs are all negative, i.e. these reactions are all exothermic.

Activation energies (Fig. 4) obtained at the B3LYP/6-31G* and B3LYP/gen levels have similar variation trends. From Fig. 4, we can see that $E_{a,1}$ of HN_5 (88.36 kJ/mol) is obviously smaller than that of the isolated N_5^- (121.14 kJ/mol). So HN_5 is less stable than N_5^- in thermodynamics, and it decomposes into HN_3 and N_2. $E_{a,1}$ of NaN_5 (100.41 kJ/mol) is higher than that of HN_5 but lower than that of N_5^-, and the final products are NaN_3 and N_2.

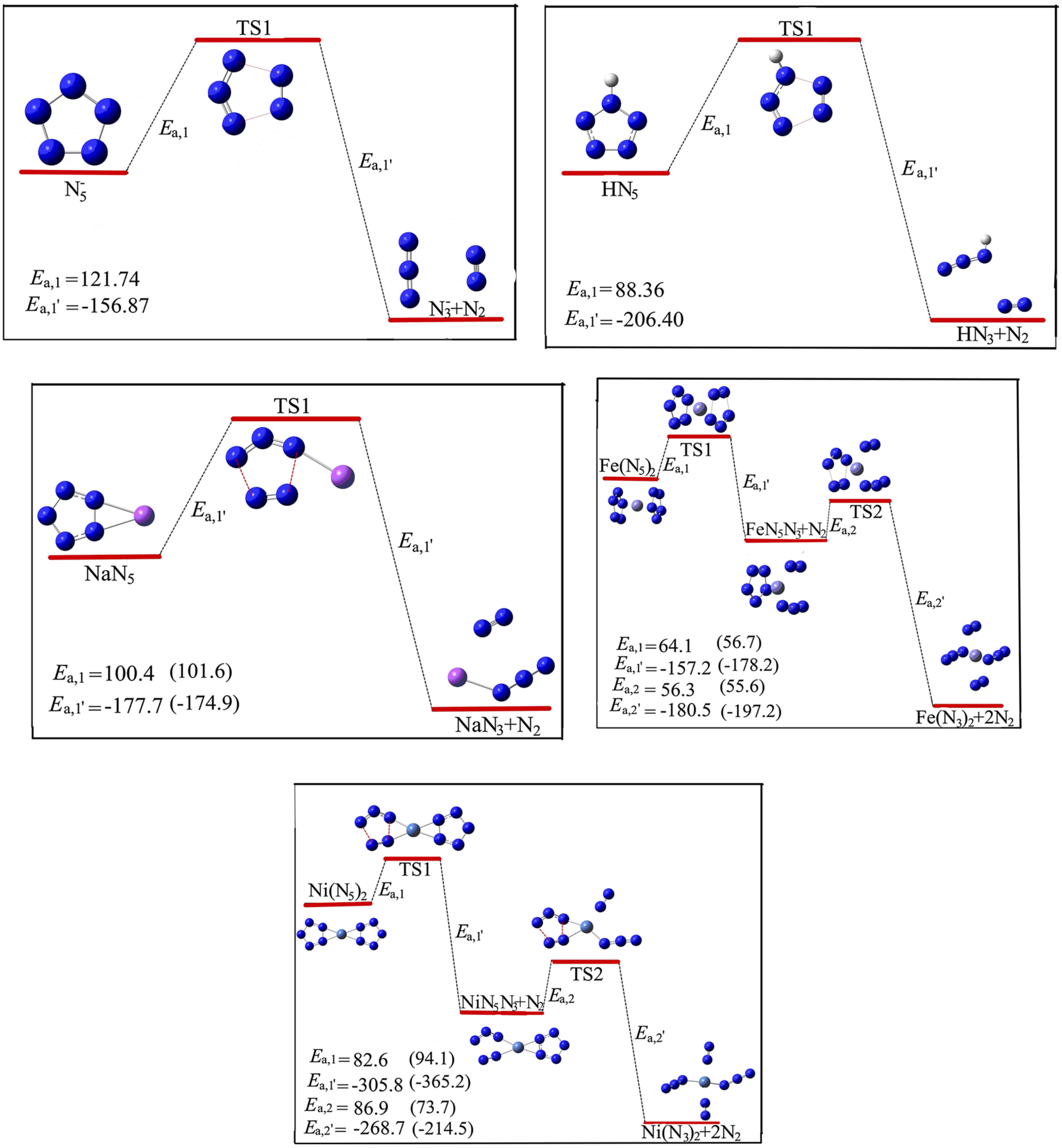


Fig. 4 Decomposition processes and activation energies (in kJ/mol) at the B3LYP/6-31G* and B3LYP/gen (values in parentheses) levels

Table 2 Activation enthalpies and free energies ($\Delta H^{\neq}$ and $\Delta G^{\neq}$), and changes in enthalpy and free energy (ΔH and ΔG) of the pyrolysis reactions obtained at the B3LYP/6-31G* level

Reaction	$\Delta H^{\neq}$ (kJ/mol)	$\Delta G^{\neq}$ (kJ/mol)	ΔH (kJ/mol)	ΔG (kJ/mol)
$N_5^- = N_3^- + N_2$	114.2	111.5	−38.9	−53.9
$HN_5 = HN_3 + N_2$	79.1	75.8	−131.4	−153.4
$NaN_5 = NaN_3 + N_2$	93.3	90.9	−80.7	−96.6
$Fe(N_5)_2 = FeN_5N_3 + N_2$	58.7	53.3	−94.3	−106.5
$FeN_5N_3 = Fe(N_3)_2 + N_2$	51.0	50.5	−124.8	−135.0
$Ni(N_5)_2 = NiN_5N_3 + N_2$	75.5	78.5	−225.2	−237.9
$NiN_5N_3 = Ni(N_3)_2 + N_2$	79.6	82.7	−183.9	−191.2

Decompositions of $Fe(N_5)_2$ and $Ni(N_5)_2$ consist of two steps, and two TSs are involved in the pyrolysis process. The TS of the first step (TS1) has the structure of $MN_5N_3\cdots N_2$ (M = Fe, Ni, see Fig. 4) and the products are N_2 and MN_5N_3. The TS of the second step (TS2) is $M(N_3)_2\cdots N_2$ and the products are N_2 and $M(N_3)_2$. The activation energies for the first ($E_{a,1}$) and second ($E_{a,2}$) steps of $Fe(N_5)_2$ are 64.15 (56.7) and 56.34 (55.6) kJ/mol from the B3LYP/6-31G* (B3LYP/gen) calculations, respectively. Pyrolysis of the second N_5 ring is easier than the first one, so decomposition of the first ring lowers the stability of the rest ring. $E_{a,1}$ and $E_{a,2}$ of $Ni(N_5)_2$ are 79.65 (94.1) and 82.66 (73.7) kJ/mol, respectively. $E_{a,1}$s and $E_{a,2}$s of $Fe(N_5)_2$ and $Ni(N_5)_2$ are all lower than the $E_{a,1}$ of the isolated N_5^-. The stabilities of the species decrease in the order of $N_5^- > NaN_5 > HN_5 > Ni(N_5)_2 > Fe(N_5)_2$. In gas phase, the stability of the isolated N_5^- is the highest, i.e. the cations H^+, Na^+, Fe^{2+} and Ni^{2+} all lower the thermal stability of N_5^-.

Herein, $E_{a,1}$s of NaN_5, $Ni(N_5)_2$ and $Fe(N_5)_2$ were computed in gas phase, while these salts should exist in solid under the normal condition. Sublimation energy should be required when the solid salts convert into the gaseous molecules. So the initial pyrolysis energy (E_p) required for the solid salt should be the sum of ΔH_{sub} and $E_{a,1}$. The method proposed by Politzer et al. [42, 43] was employed to roughly predict ΔH_{sub}s of these salts. In order to assess the reliability of this method for metallic compounds, ΔH_{sub} of ferrocene ($Fe(C_5H_5)_2$), a compound with the similar structure and experimental ΔH_{sub} available, was calculated using the same method. The obtained value (63.0 kJ/mol) is about 8.5–10.5 kJ/mol smaller than the experimental data (71.5–73.5 kJ/mol) [46–48]. Therefore, the calculated ΔH_{sub}s of NaN_5, $Fe(N_5)_2$ and $Ni(N_5)_2$ may be also somewhat smaller than their experimental values. The related parameters for evaluating ΔH_{sub}s and the obtained ΔH_{sub}s and E_ps are listed in Table 3. The stabilities of the solid salts have the order (E_p in kJ/mol) of NaN_5 (233.19) > $Ni(N_5)_2$ (161.38) > $Fe(N_5)_2$ (106.80), same to that in gas phase. The solid NaN_5 and $Ni(N_5)_2$ have acceptable stabilities.

The transition state theory (TST) was used to predict the reaction rate constant (k) at 200–500 K with the KiSThelP program [49]. All ks (in Table 4) increase with the increasing temperature, which means that the high temperature accelerates the thermal dissociation of these title molecules. For the initial decomposition reactions of the title compounds, ks have the order of $N_5^- > NaN_5 > HN_5 > Ni(N_5)_2 > Fe(N_5)_2$, which reveals that the introduced cations speed up the decomposition of N_5^-. NaN_5, HN_5 and $Ni(N_5)_2$ have the ks which are obviously smaller than 1 at the room temperature; it can be concluded that these three molecules have acceptable kinetic stabilities. ks of decompositions of $Fe(N_5)_2$ and $Fe(N_3)_2$ are quite large at 298 K, so decompositions of $Fe(N_5)_2$ and $Fe(N_3)_2$ are fast under the normal condition. In a word, NaN_5 and $Ni(N_5)_2$ have the appropriate stability in thermodynamics and kinetics.

Table 3 Predicted A_s, σ^2_{tot}, v, ΔH_{sub} and E_p at the B3LYP/6-31G* level

Compound	A_s (Å^2)	σ^2_{tot} (kJ/mol)^2	v	ΔH_{sub} (kJ/mol)	E_p (kJ/mol)
NaN_5	100.11	50026.8	0.06	132.8	233.2
$Fe(N_5)_2$	148.66	1442.2	0.11	42.6	106.8
$Ni(N_5)_2$	165.74	3502.5	0.15	78.7	161.4
$Fe(C_5H_5)_2$	182.62	745.8	0.21	63.0	

ΔH and ΔG of formation reaction and decomposition reaction

The changes in thermodynamic properties (ΔHs and ΔGs) of the formation reactions can give us information on, e.g. whether these reactions are exothermic and whether they can proceed in thermodynamics. ΔHs and ΔGs of the formation reactions of the title compounds formed by N_5^- and cations (H^+, Na^+, Fe^{2+} and Ni^{2+}) are presented in Table 5. All ΔHs are significantly negative, i.e. these reactions are exothermic and the released energies are considerable, especially the formation reactions of $Fe(N_5)_2$ and $Ni(N_5)_2$ whose cations are divalent. ΔGs are also significantly negative, so these formation reactions are spontaneous. This implies that the title compounds are easily prepared by the isolated ions. The absolute values of ΔHs and ΔGs of

Table 4 Predicted *k*s (in s^{-1}) of the title compounds at 200–500 K

Reaction	200 K	298 K	300 K	400 K	500 K
$N_5^- = N_3^- + N_2$	2.51×10^{-17}	2.81×10^{-7}	3.94×10^{-7}	3.48×10^{-2}	43
$HN_5 = HN_3 + N_2$	5.24×10^{-8}	3.94×10^{-1}	4.90×10^{-1}	1.79×10^{3}	2.69×10^{5}
$NaN_5 = NaN_3 + N_2$	3.94×10^{-12}	7.22×10^{-4}	9.34×10^{-4}	14.7	5.19×10^{2}
$Fe(N_5)_2 = FeN_5N_3 + N_2$	2.23×10^{-2}	3.21×10^{3}	3.77×10^{3}	1.78×10^{6}	7.52×10^{7}
$FeN_5N_3 = Fe(N_3)_2 + N_2$	3.02×10^{-1}	9.84×10^{3}	1.14×10^{4}	2.48×10^{6}	6.63×10^{7}
$Ni(N_5)_2 = NiN_5N_3 + N_2$	2.57×10^{-8}	1.10×10^{-1}	1.35×10^{-1}	3.57×10^{2}	4.30×10^{4}
$NiN_5N_3 = Ni(N_3)_2 + N_2$	2.11×10^{-9}	2.00×10^{-2}	2.5×10^{-2}	9.94	1.54×10^{4}

the formation reactions of HN_5 and NaN_5 have the order of $HN_5 > NaN_5$. This is because the covalent N–H bond is formed in HN_5 which results in release of a large number of heats. The order of the absolute values of ΔHs and ΔGs of $Fe(N_5)_2$ and $Ni(N_5)_2$ is in accordance with the order of their thermal stabilities, i.e. $Ni(N_5)_2 > Fe(N_5)_2$.

The changes in enthalpy and free energy of decomposition reactions of NaN_5, $Fe(N_5)_2$ and $Ni(N_5)_2$ at 298.15 K and 1.0 atm were evaluated using the following reactions:

$$NaN_5 = 2.5N_2 + Na,$$

$$Fe(N_5)_2 = 5N_2 + Fe,$$

$$Ni(N_5)_2 = 5N_2 + Ni.$$

It is obvious from Table 5 that these decomposition reactions have big negative ΔGs, so they are spontaneous. These decomposition reactions have big negative ΔHs too. The large negative ΔH means the high-energy content of these salts, they may be used as energetic compounds. The absolute values of ΔHs have the order of $Fe(N_5)_2 > Ni(N_5)_2 > NaN_5$, i.e. $Fe(N_5)_2$ releases the maximum heats. Since $Ni(N_5)_2$ has the large negative ΔH and acceptable stability, it should be the preferred one as energetic material in comparison with NaN_5 and $Fe(N_5)_2$.

Chemical stability and electron transfer

The energy gap (E_g) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is a conventional index to measure the chemical stability. A larger gap is associated with a higher chemical stability because it is energetically unfavourable to add electrons to LUMO and to extract electrons from HOMO [50]. The computed energies of HOMO and LUMO (E_{HOMO} and E_{LUMO}) and E_gs are listed in Table 6. The values of E_{HOMO} and E_{LUMO} of the title compounds are smaller than that of N_5^-, so cations lower the frontier orbital energies of N_5^-. Decreases caused by cations in E_{LUMO}s are larger than that in E_{HOMO}s, so E_gs of these compounds are smaller than that of N_5^- and have the order of $HN_5 > NaN_5 > Fe(N_5)_2 > Ni(N_5)_2$. E_gs of salts are obviously smaller than that of the covalent molecule HN_5.

Natural bond orbital analysis provides an efficient way to investigate the atomic charge distributions in molecular systems. NBO analysis results in Fig. 2 reveal that the charge on each N of N_5^- is −0.200 e. When N_5^- combines with a cation, electrons on N_5^- transfer to the cation. The transferred electrons (ΔQs) are tabulated in Table 6. ΔQ of HN_5 is considerably larger than that of NaN_5, because the N–H covalent bond is formed in HN_5. For HN_5, the N connected with H has the most negative charge (−0.201 e) which is even more than −0.200 e, this hints that the N connected with H attracts electrons from other N atoms. Charges distributed on the ortho-position Ns (−0.049 e) and meta-position Ns (−0.080 e) are less than −0.200 e. In other words, ortho-position and meta-position Ns both contribute electrons, and the ortho-position Ns do more contributions than the meta-position Ns. The similar

Table 6 Predicted E_{HOMO}, E_{LUMO}, E_g and ΔQ

Compound	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)	ΔQ (e)
N_5^-	−2.17	6.10	8.27	
HN_5	−9.08	−1.68	7.40	0.550
NaN_5	−7.32	−2.21	5.10	0.079
$Fe(N_5)_2$	−9.24	−4.32	4.92	1.202
$Ni(N_5)_2$	−9.23	−5.80	3.43	0.693

Table 5 Predicted ΔHs and ΔGs of the formation and decomposition reactions at the B3LYP/6-31G* level

Formation reaction	ΔH (kJ/mol)	ΔG (kJ/mol)	Decomposition reaction	ΔH (kJ/mol)	ΔG (kJ/mol)
$N_5^- + H^+ = HN_5$	−1362.0	−1330.4			
$N_5^- + Na^+ = NaN_5$	−533.2	−502.5	$NaN_5 = 2.5N_2 + Na$	−201.9	−298.5
$2N_5^- + Fe^{2+} = Fe(N_5)_2$	−1979.0	−1882.4	$Fe(N_5)_2 = Fe + 5N_2$	−748.9	−973.6
$2N_5^- + Ni^{2+} = Ni(N_5)_2$	−2514.7	−2439.0	$Ni(N_5)_2 = Ni + 5N_2$	−581.2	−789.2

situations happen to the charge distributions of NaN_5 and $Ni(N_5)_2$. For $Fe(N_5)_2$, the charges distributed on the ring Ns (-0.08 e) are even, i.e. every N contributes the identical number of electrons to Fe^{2+}. Inspecting the conformations and the atomic charge distributions of these molecules reveals that the structure of type II makes the N of N_5 ring contribute identical electrons to the cation, while the structure of type I results in different charge distributions. In addition, the order of ΔQs is $NaN_5 < HN_5$ and $Ni(N_5)_2 < Fe(N_5)_2$, which are completely contrary to the order of their thermal stabilities. This is because when less electrons transfer from the N_5 anion to the cation, the stability of the N_5 ring in the salts is more close to that of the isolated N_5^-. In addition, the smaller ΔQ leads to the stronger ionic interactions between the cation and anion, which should be beneficial to stable salts.

Zhang [51] proposed that the more negative the charge on the azido group of the metal-azide compound is, i.e. the less electron transfers between the metallic cation and azide anion, the lower impact sensitivity the compound has. Similarly, the more negative charge on the N_5 ring may imply the more stable metal-pentazole salt to impact.

Conclusion

Structure II is more energetically favoured for $Fe(N_5)_2$, while for other salts, I is more favourable. The thermal and kinetic stabilties have the same order of $N_5^- > NaN_5 > HN_5 > Ni(N_5)_2 > Fe(N_5)_2$ in gas phase. Although the introduced cations lower the stability of N_5^-, the stabilities of NaN_5 and $Ni(N_5)_2$ are acceptable. The pyrolysis products of the title compounds are N_2 and azido salts. The chemical stabilties (E_g, eV) of them are N_5^- (8.27) > HN_5 (7.40) > NaN_5 (5.10) > $Fe(N_5)_2$ (4.92) > $Ni(N_5)_2$ (3.43). The bigger heat release in the formation reaction and the smaller electron transfer between the cation and anion generally correspond to the more stable salt in thermodynamics.

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