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Article

Synthesis and Properties of Two Energetic Salts Based on 1-Amino-2-nitroguanidine

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Dois materiais energéticos, ricos em nitrogênio, baseados em 1-amino-2-nitroguanidina foram sintetizados. O comportamento térmico, propriedades termo-dinâmicas, estruturas eletrônicas e propriedades de detonação foram investigados. As curvas de calorimetria exploratória diferencial (DSC) mostram que 1-amino-2-nitroguanidina 2,4,5-trinitroimidazol (sal 1) pode ser usado como lançador de explosivos. Essas curvas permitem a determinação dos parâmetros termodinâmicos medidos como energia de ativação (E_k, sal 1, 282,1 kJ mol^{-1}; sal 2, 116,2 kJ mol^{-1}; E_o, sal 1, 275,0 kJ mol^{-1}; sal 2, 116,9 kJ mol^{-1}), entropia de ativação ($\Delta S^{\neq}$, sal 1, 395,7 J mol^{-1} K^{-1}; sal 2, 5,8 J mol^{-1} K^{-1}), entalpia de ativação ($\Delta H^{\neq}$, sal 1, 278,7 kJ mol^{-1}; sal 2, 113,1 kJ mol^{-1}), energia livre de ativação ($\Delta G^{\neq}$, sal 1, 117,6 kJ mol^{-1}; sal 2, 110,9 kJ mol^{-1}), calor de formação (ΔH_f^0, sal 1, 264,7 kJ mol^{-1}; sal 2, 487,6 kJ mol^{-1}), temperatura crítica de explosão térmica (T_b, sal 1, 412,3 K; sal 2, 388,9 K) implicam que os sais sintetizados são seguros o suficiente durante o estoque ou uso; em vista da pressão de detonação (P, sal 1, 30,2 GPa; sal 2, 29,1 GPa) e da velocidade de detonação (D, sal 1, 8398 m s^{-1}; sal 2, 8334 m s^{-1}), acredita-se que os dois sais baseados em 1-amino-2-nitroguanidina possuem potencial para serem usados como materiais energéticos.

Two nitrogen-rich energetic materials based on 1-amino-2-nitroguanidine were synthesized. The thermal behavior, thermodynamic properties, electron structures and detonation properties were investigated. The dynamic (DSC) curves show that 1-amino-2-nitroguanidinium 2,4,5-trinitroimidazole (salt 1) can be used as cast explosives. These curves allow determination of their melting points and thermodynamic parameters such as activation energy (E_k, salt 1, 282.1 kJ mol^{-1}; salt 2, 116.2 kJ mol^{-1}; E_o, salt 1, 275.0 kJ mol^{-1}; salt 2, 116.9 kJ mol^{-1}), entropy of activation ($\Delta S^{\neq}$, salt 1, 395.7 J mol^{-1} K^{-1}; salt 2, 5.8 J mol^{-1} K^{-1}), enthalpy of activation ($\Delta H^{\neq}$, salt 1, 278.7 kJ mol^{-1}; salt 2, 113.1 kJ mol^{-1}), free energy of activation ($\Delta G^{\neq}$, salt 1, 117.6 kJ mol^{-1}; salt 2, 110.9 kJ mol^{-1}), heat of formation (ΔH_f^0, salt 1, 264.7 kJ mol^{-1}; salt 2, 487.6 kJ mol^{-1}) and critical temperature of thermal explosion (T_b, salt 1, 412.3 K; salt 2, 388.9 K), suggesting that the synthesized salts are safe enough during storage or usage. In view of the detonation pressure (P, salt 1, 30.2 GPa; salt 2, 29.1 GPa) and detonation velocity (D, salt 1, 8398 m s^{-1}; salt 2, 8334 m s^{-1}), it is predicted that both 1-amino-2-nitroguanidine-based salts have the potential to be the useful energetic materials.

Keywords: 1-amino-2-nitroguanidine, energetic salts, thermodynamic properties, electronic structure, detonation properties

Introduction

Modern nitrogen-rich energetic materials with excellent detonation properties and low sensitivities continue to attract considerable interests since they tend to have a reduced environment impact.[1-4] However, people found that there appear sharp contradictions among these energetic materials regarding to the high detonation performances and stabilities such as sensitivity to impact, friction, thermal shock and so on. In order to solve these problems, a focus of recent interests in energetic compounds has been the synthesis of nitrogen-rich energetic salts which exhibit a combination of high positive heats of formation, satisfactory detonation performances and low sensitivity. This is because these salt-based energetic materials often possess advantages over non-ionic molecules since these salts tend to exhibit lower vapor pressures and higher densities than their atomically similar non-ionic analogues.[5]

Guanidine and its derivatives such as aminoguanidine, diaminoguanidine and triaminoguanidine, were often

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selected as the nitrogen-rich cations in the previous research.[6,7] However, little investigation was reported on 1-amino-2-nitroguanidine, which has superior detonation velocity and detonation pressure to those of guanidine derivatives.[8] It is predicted that the 1-amino-2-nitroguanidine-based energetic salts may have potentially broad application in the fields of explosives. On the other hand, poly-nitro anion containing a large number of inherently energetic C-N and N-N bonds, have been the preferred selections for scientists since these types of compounds will help improve the heat of formation during the decomposition process. Obviously, 2,4,5-trinitroimidazole[9] and 5-nitrotetrazole[10] are the compounds of this type with *N*-heterocyclic ring and a large number of C-N or N-N bonds in the molecular. For the above reasons, two 1-amino-2-nitroguanidine-based nitrogen-rich energetic salts were designed and synthesized (Scheme 1). The thermal behavior, electron structure and detonation properties were also investigated to give a better understanding of their physical and chemical properties.

Experimental

^{1}H and ^{13}C nuclear magnetic ressonance (NMR) spectra of the 1-amino-2-nitroguanidine-based salts were obtained by a Bruker Avance III 500 MHz spectrometer; infrared (IR) spectra were performed on a Thermo Nicolte IS10 IR instrument; electrospray ionization mass spectrometry (ESI-MS) results were obtained from a Finnigan TSQ Quantum Mass Spectrometer and all the thermodynamic tests were performed on a NETZSCH STA 409 PC/PG system with an innitial mass of 3.0 mg were placed in alumina crucibles with high-purity nitrogen.

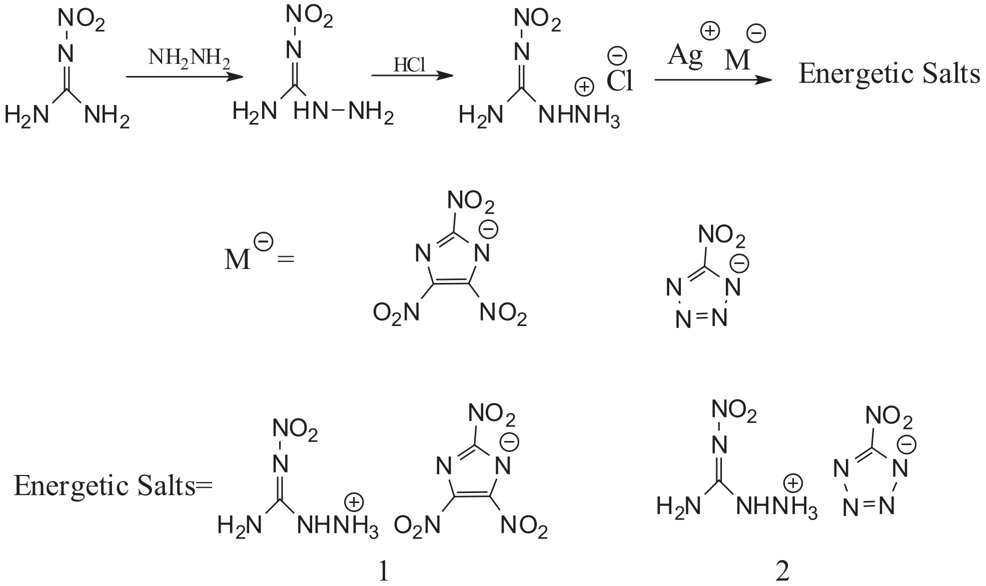
Computations were performed with the Gaussian 03 suite of programs[11] using B3LYP functional with 6-31+G(d,p) basis set. Input geometric structures of these salts were based on the optimum configuration that obtained by Hyperchem software. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.

Results and Discussion

The thermogravimetry (TG)-derivative thermogravimetry (DTG)-differential scanning calorimetry (DSC) curves of 1-amino-2-nitroguanidinium 2,4,5-trinitroimidazole salt (a), and 1-amino-2-nitroguanidinium 5-nitrotetrazole salt (b) with the initial temperature of 35 °C up to 500 °C at the heating rate of 10 °C min^{-1} were shown in Figure 1.

From TG curves, it is obviously seen that the decomposition of the two salts were a two-stage process with approximately 90% weight loss. Accordingly, some evident or faint peaks were also found, which were corresponding to the two-stage decomposition process in the TG curves. In view of the DSC curves, both of salts 1 and 2 have an evident sharp exothermic peak. On the other hand, salt 1 has the melting point which indicate that the 1-amino-2-nitroguanidinium 2,4,5-trinitroimidazole salt has a potential to be cast explosives. Based on the curves, it is predicted that all the salts have potential application as primary explosive.

Kissinger[12] and Ozawa's[13] method are two important ways to investigate the thermodynamic properties of an energetic material.



Scheme 1. Synthetic route of the energetic salts.

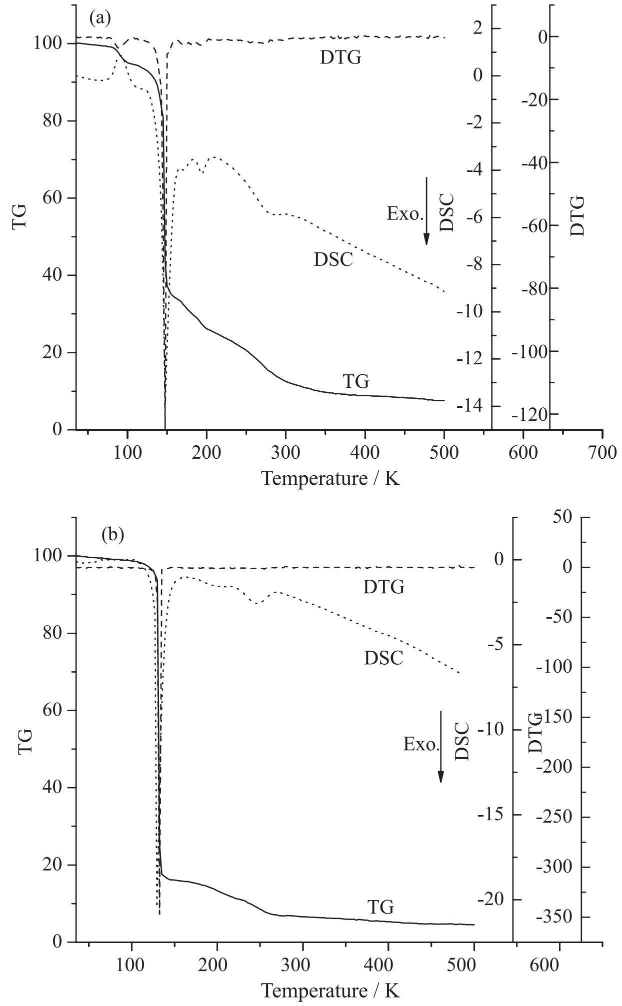


Figure 1. TG-DTG-DSC curves of the title salts at a heating rate of 10 °C min^{-1}.

Kissinger's method:[12]

$$\ln\frac{\beta_i}{T_{pi}^2} = \ln\frac{A_K R}{E_K} - \frac{E_K}{RT_{pi}} \tag{1}$$

Ozawa's method:[13]

$$\log\beta = const. - 0\ 4567\frac{E_0}{RT} \tag{2}$$

where, β is the heating rate; T_{pi} is the maximum peak temperature; R is the gas constant; E_k and E_o are the activation energy calculated by the Kissinger and Ozawa's methods, respectively. To obtain the relative kinetic parameters such as activation energy (E), pre-exponential constant (A), entropy of activation ($\Delta S^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$), free energy of activation ($\Delta G^{\neq}$) and the critical temperature of thermal explosion (T_b), equation 3-7 were employed:[14]

$$T_{p_i} = T_{p0} + b\beta_i + c\beta_i^2 + d\beta_i^3 \tag{3}$$

$$A = (\frac{k_B T}{h})\exp(\frac{\Delta S^{\neq}}{R}) \tag{4}$$

$$\Delta H^{\neq} = E_k - RT \tag{5}$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \tag{6}$$

$$T_b = \frac{E_0 - \sqrt{E_0^2 - 4E_0RT_{p0}}}{2R} \tag{7}$$

where $T = T_{p0}$, the peak temperature (T_{pi}) corresponding to $\beta \rightarrow 0$; E_k, calculated by Kissinger's method; $A = A_k$, calculated by Kissinger's method; k_B, the Boltzmann constant, 1.3807×10^{-23}J K^{-1}; h, the Plank constant, 6.626×10^{-34}J s^{-1}.

Values of the relative kinetic parameters were tabulated in Table 1. It is obviously seen the calculated apparent activation energy (E) by Kissinger and Ozawa's methods are approximately the same and the linear correlation coefficients (r) are very close to 1, which indicates that the results are credible enough. The measured thermodynamic parameters such as activation energy (E_k, salt 1, 282.1 kJ mol^{-1}; salt 2, 116.2 kJ mol^{-1}; E_o, salt 1,275.0 kJ mol^{-1}; salt 2, 116.9 kJ mol^{-1}), entropy of activation ($\Delta S^{\neq}$, salt 1, 395.7 J mol^{-1} K^{-1}; salt 2, 5.8 J mol^{-1} K^{-1}), enthalpy of activation ($\Delta H^{\neq}$, salt 1, 278.7 kJ mol^{-1}; salt 2, 113.1 kJ mol^{-1}), free energy of activation ($\Delta G^{\neq}$, salt 1, 117.6 kJ mol^{-1}; salt 2, 110.9 kJ mol^{-1}) involves that salt 2 is less stable compared with the salt 1, since it has the lowest activation energy and enthalpy of activation. In view of the critical temperature of thermal explosion (T_b), salt 1 (412.3 K) is higher than that of salt 2 (388.9 K), which also demonstrated that salt 1 is much more stable than salt 2. Besides, the values of T_b of the two salts are relative high and meet the security requirements during storage or use.

Table 1. Calculated data of the kinetic parameters for the main exothermic decomposition reaction of the title salts

Salt No.	Kissinger method			Ozawa method		T_{p0} / K	T_{b} / K	Thermodynamic parameters		
	E_{k} / (kJ mol^{-1})	log A / (s^{-1})	r_{k}	E_{o} / (kJ mol^{-1})	r_{o}			$\Delta S^{\neq}$ / (J mol^{-1} K^{-1})	$\Delta H^{\neq}$ / (kJ mol^{-1})	$\Delta G^{\neq}$ / (kJ mol^{-1})
1	282.1	33.6	0.998	275.0	0.998	407.2	412.3	395.7	278.7	117.6
2	116.2	13.2	0.998	116.9	0.998	378.1	388.9	5.8	113.1	110.9

The molecular orbital and the electronic structure of the two salts were investigated based on the B3LYP/6-31G(d,p) level-optimized structure. The energy gap (ΔE), which can be used for predicting the reactivity of a molecular were investigated in this paper. The calculated energy gap value of the title compounds are 5.58 eV and 4.39 eV, respectively, indicating that salt 1 may have a lower reactivity, while salt 2 has a higher reactivity. To give a better understanding of the chemical and physical properties of the title compounds, the 3D plots of the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and the molecular electrostatic potentials (MEP) were illustrated in Figure 2. It is obviously seen that most of the HOMO and LUMO levels are located in the anion and all the orbitals are 2-fold degenerated, which indicates that the removal of an electron from the HOMO level or addition of an electron to the LUMO level could weaken the skeleton framework. As for the MEPs, it is seen that most of the negative potentials appear to be distributed on the O atoms in the $-NO_2$ groups, while the positive potentials appear to be at C, N or H atoms. This may attribute to the stabilization of the molecular structure according to the law proposed by Klapötke *et al.*.[15]

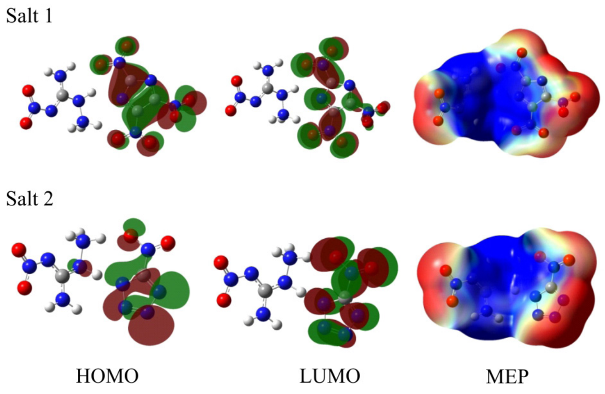


Figure 2. HOMO, LUMO, and MEP of the title compounds.

In order to give a better understanding of the thermodynamic properties of the title compounds, the standard molar heat capacity $C^0_{p,m}$, standard molar entropy S^0_m and standard molar enthalpy H^0_m from 200 to 700 K were evaluated by quantum chemistry and presented in Figure 3.

Obviously, all the thermodynamic parameters increase with the increasing of the temperature. The main reasons were as follows: when the temperature is low, the main contributions to the thermodynamic functions are from the translation and rotation of molecules while the main contributions to the thermodynamic functions are from the intensified vibrations at a higher temperature. Besides, the correlation equations between the standard molar heat capacity $C^0_{p,m}$, standard molar entropy S^0_m, standard molar enthalpy H^0_m and the temperature were also presented as follows (where R^2 is the correlation coefficients):

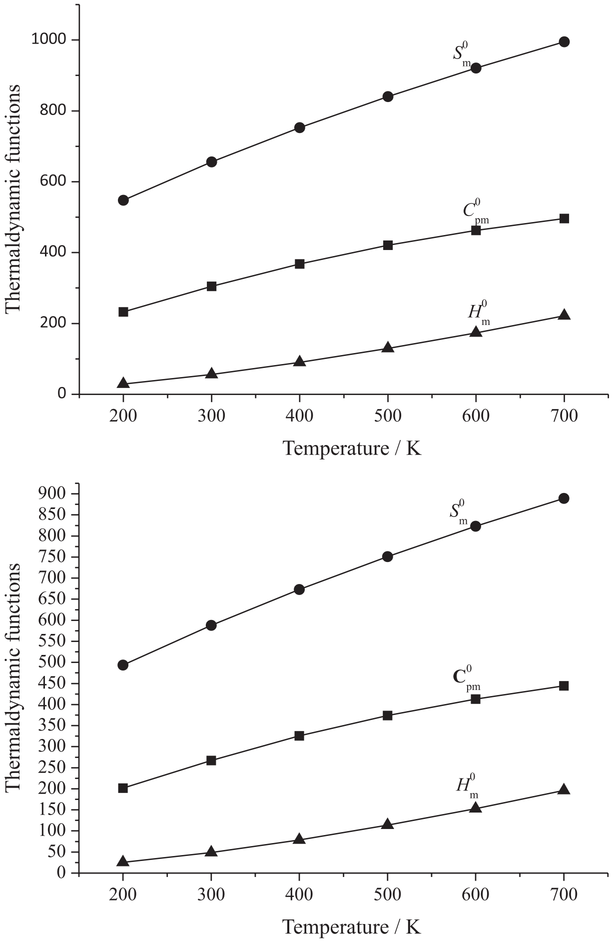


Figure 3. Relationships between the thermodynamic functions and temperature (T).

Salt 1:

$$C^{\theta}_{p,m} = 31.87 + 0.815T - 0.00041T^2 \qquad R^2 = 0.9999$$

$$S^{\theta}_{m} = -255.99 + 0.840T - 0.00022T^2 \qquad R^2 = 0.9999$$

$$H^{\theta}_{m} = -9.61 + 0.098T + 0.00021T^2 \qquad R^2 = 0.9998$$

Salt 2:

$$C^{\theta}_{p,m} = 49.91 + 0.716T - 0.00034T^2 \qquad R^2 = 0.9999$$

$$S^{\theta}_{m} = 287.15 + 0.936T - 0.00030T^2 \qquad R^2 = 0.9999$$

$$H^{\theta}_{m} = -6.74 + 0.102T + 0.00021T^2 \qquad R^2 = 0.9999$$

The semi-empirical Kamlet-Jacobs equations[16] were often employed when the detonation properties, (detonation velocity, D and detonation pressure, P) were predicted and has been demonstrated as a reliable way. It was written as follows:

$$D = 1.01(N\overline{M}^{1/2}Q^{1/2})^{1/2}(1+1.3\rho) \qquad (8)$$

$$P = 1.558\,\rho^2 N\overline{M}^{1/2}Q^{1/2} \qquad (9)$$

Table 2. Formulas for calculating the values of N, M, and Q for an explosive $C_aH_bO_cN_d$

Parameter	Stoichiometric ratio		
	$C \geq 2a + b/2$	$2a + b/2 > c \geq b/2$	$b/2 > c$
N	$(b + 2c + 2d)/4M$	$(b + 2c + 2d)/4M$	$(b + d)/2M$
$\overline{M}$	$4M/(b + 2c + 2d)$	$(56d + 88c - 8b)/(b + 2c + 2d)$	$(2b + 28d + 32c)/(b + d)$
$Q*10^{-3}$	$(28.9b + 94.05a + 0.239\Delta H_f)/M$	$[28.9b + 94.05(c/2 - b/4) + 0.239\Delta H_f]/M$	$(57.8c + 0.239\Delta H_f)/M$

[a]a, b, c stand for the number of C, H, O and N atoms in the explosive molecule, respectively; [b]M in the formula is the molecular weight of the explosive (g mol^{-1}); ΔH_f is the heat of formation of the explosive (kJ mol^{-1}).

where D, the detonation velocity (km s^{-1}); P, the detonation pressure (GPa); N, the moles of detonation gases per gram explosive; $\overline{M}$, the average molecular weight of these gases; Q, the heat of detonation (cal g^{-1}); ρ, the density of explosives (g cm^{-3}) that obtained according to the reference method;[17] and N, $\overline{M}$, and Q were calculated by the equations that summarized in Table 2.

Based on the equations in Table 2, the heat of formation (ΔH_f^0) of the salts should be known first to calculate the detonation velocity and detonation pressure. Then the Born-Haber energy cycle (Figure 4), isodesmic reactions (Scheme 2) and equations 10-12[18] were joined together to calculate the accurate values of heat of formation. However, it also should be pointed out that the enthalpy of the isodesmic reaction (ΔH_f^0) is obtained by combining the MP2/6-311++G** energy difference, the zero-point energies (B3LYP/6-31+G**), and other thermal factors (B3LYP/6-31+G**).

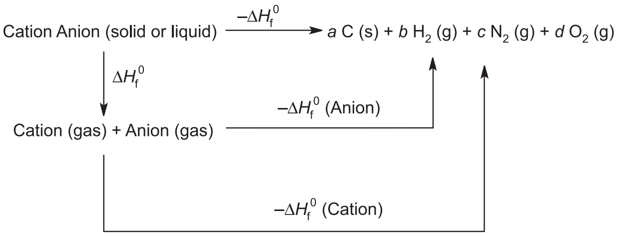


Figure 4. Born-Haber cycle for the formation of energetic salts. a, b, c and d are the number of moles of the respective products.

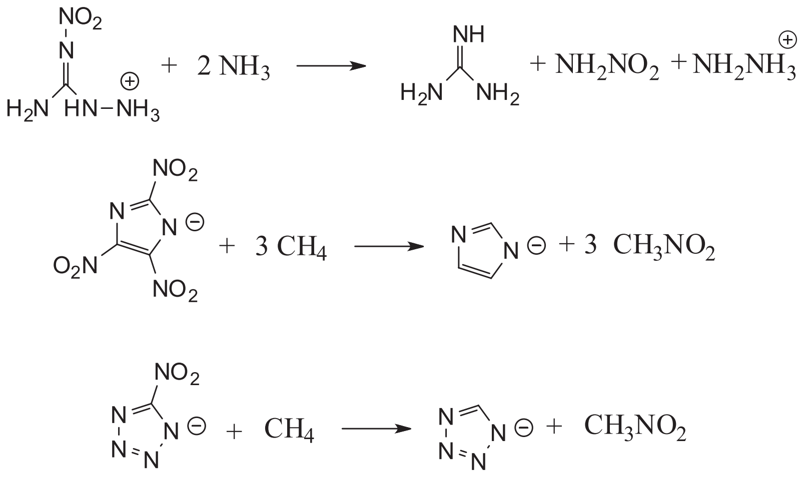
$$\Delta H_f^0(\text{ionic salt, 298 K}) = \sum \Delta H_f^0(\text{cation, 298 K}) + \sum \Delta H_f^0(\text{anion, 298 K}) - \Delta H_L \quad (10)$$

$$\Delta H_L = U_{POT} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT \quad (11)$$

$$U_{POT}(\text{kJ mol})^{-1} = 1981.2(\rho/M)^{1/3} + 103.8 \quad (12)$$

where ΔH_L is the lattice energy of the salts; U_{POT} is the lattice potential energy; p and q are the charge number of the cation and anion; n_M and n_X are equal to 6, according to reference 18.

The values for the calculated detonation were summarized and tabulated in Table 3. It is seen that all the salts have high positive heat of formation (salt 1, 264.7 kJ mol^{-1}; salt 2, 487.6 kJ mol^{-1}) which are benefit to the detonation velocity and detonation pressure. The calculated P (salt 1, 30.2 GPa; salt 2, 29.1 GPa) and D (salt 1, 8398 m s^{-1}; salt 2, 8334 m s^{-1}) indicates that the detonation performance of the salts are superior to those of trinitrotoluene (TNT) and are equal to those of 2,4,6-triamino-1,3,5- trinitrobenzene (TATB). Besides, the



Scheme 2. Isodesmic reactions for calculations of heats of formation.

Table 3. Detonation values of the title salts

Salt	Dens.[a]	$\Delta H_{f\ \text{cation}}^{0}$ [b]	$\Delta H_{f\ \text{anion}}^{0}$ [c]	$\Delta H_{f\ \text{lattice}}^{0}$ [d]	$\Delta H_{f\ \text{salt}}^{0}$ [e]	P[f]	D[g]	OB[h]	N%[i]	T_m[k]	T_d[l]
1	1.70	862.0	−148.5	448.8	264.7	30.2	8398	−14.9	43.58	83.2	143.0
2	1.64	862.0	112.8	487.6	487.2	29.1	8334	−20.5	59.82	–	121.6
TNT[j]	1.65	–	–	–	–	19.5	6881	−24.7	18.50	80.4	295
TATB[j]	1.94	–	–	–	–	31.2	8114	−18.6	32.55	–	318

[a]Density (g cm^{-3}) which were obtained according to reference 19; [b]calculated molar enthalpy of formation of the cation (kJ mol^{-1}); [c]calculated molar enthalpy of formation of the anion (kJ mol^{-1}); [d]calculated molar lattice energy (kJ mol^{-1}); [e]calculated molar enthalpy of formation of the salt (kJ mol^{-1}); [f]detonation pressure (GPa); [g]detonation velocity (m s^{-1}); [h]oxygen balance (OB), an index of the deficiency or excess of oxygen in a compound required to convert all C into CO_2 and all H into H_2O; for the compound with molecular formula $C_aH_bN_cO_d$ (without crystal water), OB (%) = 1600 (d − 2a − b/2)/M_w (%); [i]nitrogen content; [j]data from reference 20; [k]the melting temperature (°C); [l]thermal decomposition temperature (°C) under nitrogen gas (DSC, 5 °C min^{-1}).

oxygen balance is closer to zero and the nitrogen content is also higher compared with those of TNT and TATB. Based on the above-described data, it is predicted that the two 1-amino-2-nitroguanidinium-based salts have the potential to be useful energetic material in primary explosives and gas generating agent.

Conclusions

The decomposition of the salts are a two-stage of process with approximately 90% weight loss. Salt 1 can be used as cast explosives. The measured thermodynamic parameters are as follows: activation energy (E_k, salt 1, 282.1 kJ mol^{-1}; salt 2, 116.2 kJ mol^{-1}; E_o, salt 1, 275.0 kJ mol^{-1}; salt 2, 116.9 kJ mol^{-1}), entropy of activation ($\Delta S^{\neq}$, salt 1, 395.7 J mol^{-1} K^{-1}; salt 2, 5.8 J mol^{-1} K^{-1}), enthalpy of activation ($\Delta H^{\neq}$, salt 1, 278.7 kJ mol^{-1}; salt 2, 113.1 kJ mol^{-1}), free energy of activation ($\Delta G^{\neq}$, salt 1, 117.6 kJ mol^{-1}; salt 2, 110.9 kJ mol^{-1}), critical temperature of thermal explosion (T_b, salt 1, 412.3 K; salt 2, 388.9K).

The calculated energy gap value of the title compounds are 5.58 eV and 4.39 eV, respectively, and salt 1 may have a lower reactivity while salt 2 has a higher reactivity. The molecular orbital and the electronic structure of the salts also meet the requirements of stability.

All the salts have high positive heat of formation (salt 1, 264.7 kJ mol^{-1}; salt 2, 487.6 kJ mol^{-1}). The high detonation velocity (salt 1, 8398 m s^{-1}; salt 2, 8334 m s^{-1}) and detonation pressure (salt 1, 30.2 GPa; salt 2, 29.1 GPa) involves that the title salts have superior detonation properties than those of TNT and TATB.

Supplementary Information

Supplementary Information (NMR, FTIR and ESI-MS spectra) is available free of charge at http://jbcs.sbq.org.br.

Acknowledgements

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