Theoretical Analysis on Common Stabilizers for Nitrate Solid Propellants[*]

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[ABSTRACT]　Density functional theory (DFT) B3LYP method and 6-311G[*] basis set were employed to study 19 kinds of stabilizers in nitrate solid propellant, including newly developed AK2, M1-M5, STAB-1, and normal aromatic amine stabilizers, such as o-nitrodiphenylamine (2-NDPA), diphenylamine (DPA), dimethyldiphenyl urea (C2), diethyl diphenyl urea (EC), and N-(2-methoxyethyl) p-nitroaniline (MENA). Calculations were conducted in acidity and basicity, dissociation energy (2.68-4.85 eV), Wiberg bond indexes (WBI) and nucleus-independent chemical shift (NICS) (32.80-49.89), and electron affinity (0.067-0.839 eV) and energy gap (3.286-5.891 eV) to verify stabilizers' nucleophilicity, molecular stability, aromaticity and the ability to attract electrons, respectively. Based on results above, the stabilizer with the best ability can be proposed.

[KEYWORDS]　solid propellant; stabilizer; density functional theory (DFT); dissociation energy

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硝酸酯类固体推进剂常用安定剂的理论研究

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[摘　要]　采取密度泛函理论(DFT)的 B3LYP 方法和 6-311G[*]基组,计算研究了 AK2、M1-M5、STAB-1 类新型安定剂以及常用的芳香胺类安定剂的性质。包括邻硝基二苯胺(2-NDPA)、二苯胺(DPA)、二甲基二苯基脲(C2)、二乙基二苯基脲(EC)、N-(2-甲氧基乙基)对硝基苯胺(MENA)等 19 种硝酸酯类固体推进剂常用的安定剂。计算安定剂的酸碱性,比较亲核能力的强弱;计算安定剂的离解能(2.68～4.85 eV),比较其分子的稳定性;计算安定剂的最小键级(WBI)和核化学位移(NICS)(32.80～49.89),讨论其芳香性大小;计算电子亲和能(0.067～0.839 eV)和间隙能(3.286～5.891 eV),分析其吸引电子的能力。计算结果可为选择性能优良的安定剂提供理论基础。

[关键词]　固体推进剂;安定剂;密度泛函理论;离解能

Introduction

Propellant should have good safety performance to ensure that the propellant has a longer service life, and ensure that no combustion and explosion accidents occur in the storage, transportation and assembly process. At the same time, it can maintain enough sta-bility when subjected to mechanical impact. In order to prevent unexpected fire accidents, propellant should also have a higher autoignition temperature. However, due to the presence of nitrate in solid propellants and the autocatalytic decomposition reaction of nitrate during long-term storage, the free radicals of nitric oxide could be produced[1]. The generated free radicals of nitric oxide can continue to react with other com-

ponents of propellants, which accelerate the decomposition of nitrate.

The nitric acid obtained in former reaction is decomposed into NO_2. Some NO_2 reacts with nitrate and is converted to NO. After the cyclic thermal decomposition reaction, not only will the propellant reduce its own reaction function, but also heat combustion and even explosion will occur during transportation. Therefore, the stabilizer is put into nitrate and nitrate-containing propellant in order to stabilize the propellant. In this paper, 19 kinds of stabilizers for solid propellants at home and abroad were selected. Among them, AK2, M1-M5 and STAB-1 are all new stabilizers. Aromatic amine stabilizers are commonly used in nitrocotton (NC) propellants in China, such as o-nitro-diphenylamine (2-NDPA), diphenylamine (DPA), dimethyldiphenylurea (C2), diethyl-diphenylurea (EC), N-(2-methoxyethyl) p-nitroaniline (MENA) and so on.

Most of the 19 stabilizers are derivatives of aromatic amines. In the middle part of the molecule, N atoms are connected with H atoms which are more active and are more easily attracted by NO_2 produced by autocatalytic decomposition of solid propellant. Chemical stabilizers are added to reaction with these nitrogen oxides because they have a great effect on stabilizing nitrates. The absorption of nitrogen oxides can prevent the propellant from autocatalytic decomposition, and also prevent other components of solid propellant from reacting with nitrogen oxides to produce urethane or urea, thus reducing the degradation ability and mechanical pro-perties of the propellant[2].

At present, the rapid growth of computer technology has drastically changed the way in which molecular simulations and quantum chemical calculations are used to shed light on the structure of materials in depth and extensively. Quantum mechanics have been performed to investigate the microstructure and properties of matter. Our research group have reported the compatibility and the glass transition temperature of the components in solid propellant by molecular dynamics simulation[3-4]. In this study, the acidities-basicities, dissociation energy, Wiberg bond indexes (WBI), nucleus-independent chemical shift (NICS), electron affinity and energy gap of 19 stabilizers in propellant were calculated using density functional theory (DFT) B3LYP method and 6-311G* basis set. The results can provide a theoretical basis for the selection of optimized stabilizers for propellants.

1　Computational methods

Geometries optimization of stabilizer molecules were conducted without any constraint. Each optimized structure was confirmed by the frequency calculation to be the real minimum without any imaginary vibration frequency. All the calculations were implemented at B3LYP/6-311G* level using the Gaussian 09 package. In order to characterize stability of stabilizers, acid-base property, dissociation energy, bond order NICS values, electron affinity and HOMO-LUMO energy gap of the stabilizers in solvent state were calculated.

2　Results and discussion

2.1　Acid-base property

Stabilizer is used to absorb NO_2 produced by nitrate autocatalysis reactions in propellant. If the acidity of stabilizer is too high, it will affect other components in propellant. In order to absorb NO_2, stabilizer should be alkaline as far as possible, so stabilizer with higher alkalinity should be chosen. The experimental pKa of DPA at 24 ℃ is 0.78[5] and the calculated value is 0.71 at 25 ℃. The calculated result is very close to the experimental value, which provides a theoretical basis for inferring the stability effect of stabilizers.

The dissociation constant pKa of stabilizer in solvent was calculated by Gaussian method, and its acidity and basicity were compared. The calculation results in Tab. 1 show that RES has the strongest acidity, and pKa is 0.739, followed by 2-NDPA. However, 2-NDPA cannot be used alone in solid propellant because of its slow nitrification rate at the initial stage of the reaction. In addition, it is found that 2-NDPA has strong crystallization and migration defects in the performance testing of high-energy solid propellant[6]. Compared with C2, EC is more alkaline, which is due to the presence of more branch chains in EC. Similarly, PNEA has one more branch chain than PNMA and is more alkaline. Compared with MNA,

MENA has one more carbonyl group and its alkalinity decreases.

Tab. 1   pKa （25 ℃）and dissociation energy of stabilizers

Name	pKa	Dissociation energy/eV
RES	0.739	4.85
2-NDPA	0.730	3.89
M1	0.728	3.64
M5	0.726	3.69
M4	0.726	3.67
AK2	0.714	3.85
DPA	0.710	3.66
STAB1	0.699	3.51
C2	0.693	2.68
2AMP	0.686	3.66
M2	0.670	3.50
MENA	0.670	2.85
PNMA	0.662	4.52
M3	0.656	3.80
2ANP	0.648	3.76
EC	0.644	2.81
PNEA	0.634	4.48
MNA	0.633	4.49
TPA	0.633	3.24

2.2   Dissociation energy

When enough energy is available, a molecule dissociates into two groups at the weakest bond. The dissociation energy is the energy difference between the broken groups and the original molecule. The dissociation energy needed to break the bond is usually approximately expressed as the dissociation enthalpy of the bond at 298 K. The larger the dissociation energy, the more likely the free radicals bind to each other, the less likely the free ra-dicals exist alone and the less stable the free radicals are. Tab. 1 shows that the dissociation energies of amide derivatives such as C2, EC and MENA are relative small. They are only suitable for non-volatile solvent propellants, although they have no saponification effect on nitrate esters and good solubility.

Volatile solvent propellant generally contains more water, which easily leads to hydrolysis of stabilizer. Benzamide produced by hydrolysis has greater saponification ability to nitrocellulose before NO is absorbed, which is not conducive to improving the stability of pro-

pellant and explosive[7]. This is in agreement with the experimental results, that is, at 95 ℃, the decomposition ability of AK2 is better than that of C2 and DPA[8].

The experimental results show that PNMA begins to age in about 4-6 days at 80 ℃, while 2-NDPA begins to age in about 10 days. 2-NDPA reacts mainly with nitroglycerin in propellant, while, PNMA reacts with nitrogen-oxygen double bond in nitroso group[9]. Moreover, in the presence and absence of NO_2, the energy required to break an O—N bond in nitrates differs from 26 to 31 kJ/mol. NO_2 produced by the slow decomposition of nitrate during storage can autocatalyze nitrate. The dissociation energy of phenolic derivatives such as RES is greater, even twice that of the worst stabilizer. Therefore, phenol derivatives or nitroaniline derivatives, such as MNA and RES will be expected to be new stabilizers.

2.3   Aromatic property

Because 19 propellant stabilizers in our discussion are aromatic substances, their stabilities are usually observed by studying aromatic property. In the calculation of aromatic property, the most commonly used method is to detect the NICS of molecules, which calculate the center of the absolute magnetic shielding ring. The aromaticities from NICS and NMR are consistent. In this method, the antiaromaticity is expressed by a negative NICS value. It can be known from Tab. 2 that the NICS of M3 is the smallest, indicating that the aromaticity is the smallest, and the experimental data also show that the negative charge density of nitrogen atom is at the highest level, which is not conducive to the absorption of electrons[10].

It can be observed from Tab. 2 that the NICS values of M1, M3 and M4, three new stabilizers studied abroad, vary greatly with pKa, while the NICS value of M2 is at the intermediate level, which is suitable for a new stabilizer.

Tab. 2 shows the bond order of 19 stabilizers. The stabilizer with large dissociation energy, large bond order and small collision sensitivity to store easily is required[11]. Although the dissociation energy of MNA is large and its bond order is small, it is prone to explosion during storage. The experimental results show that the order of absorption rate of NO_2 and HNO_2

Tab. 2　Bond orders and NICS values of stabilizers

Name	WBI (C—N)	WBI (C—O)	WBI (N—O)	NICS
2AMP	0.316	0.663		39.11
2ANP	0.387	0.573		33.77
AK2	0.337	0.615		45.67
C2	0.355	0.590		40.35
EC	0.345	0.618		39.95
M1	0.337	0.637		35.81
M2	0.324	0.638		37.11
M3	0.333	0.632	0.293	32.80
M4	0.336	0.635	0.282	40.16
M5	0.358	0.518	0.290	40.62
MENA	0.379	0.631	0.291	43.92
2-NDPA	0.293		0.297	42.13
DPA	0.328			42.27
MNA	0.204		0.291	45.30
PNEA	0.396		0.232	45.92
PNMA	0.394		0.231	49.89
TPA	0.319			38.62
RES		0.365		49.34
STAB1				47.56

by different stabilizers is PNMA > PNEA > 2-NDPA at the initial stage of reaction with nitrate. While the order of absorption rate of anhydrous HNO_3 is 2-NDPA = PNMA > PNEA. It can be seen that the reaction of absorption of HNO_3 is different from that of absorption of NO_2 and HNO_2. The absorption mode of PNEA is similar to that of PNMA, while 2-NDPA is the absorption reactant of nitrite.

2.4　Electron affinity and energy gap

When an electron is added to another neutral atom or molecule, the energy released or consumed by the formation of negative ions in the gaseous state is called electron affinity(EA). There is a direct correlation between EA and stability[12]. Energy gap is required to promote valence electrons to combine with an atom to become conducting electrons. Because they can move freely in the lattice and conduct current as a charge carrier, the energy gap of HOMO-LUMO can be used as a basis for judging stability. The larger the EA and the energy gap are, the easier the free radicals are absorbed. However, because the stabilizer may react with nitrate or the molecular chain of the binder, the stabilizer with low EA is selected.

The results show that amide derivatives such as MENA easily react with NO_2. They can eliminate NO_2 and greatly reduce the catalytic reaction probability of NO_2 to nitrate. Therefore, they have a stabilizing effect on the decomposition of nitrate. However, new nitro-containing aniline stabilizers such as M1-M5 mentioned above have better stabilization effect on nitrate. The nitro group of stabilizer M3 has greater steric hindrance effect on active hydrogen, so M3 is more suitable for some special stabilized nitrates.

Tab. 3　EA and energy gap of stabilizers

eV

Name	EA	HOMO	LUMO	Energy gap
TPA	0.067	5.209	0.681	4.527
DPA	0.111	5.352	0.464	4.888
AK2	0.130	5.802	0.972	4.830
STAB1	0.131	5.969	0.086	5.883
M5	0.160	7.040	2.919	4.122
2ANP	0.171	7.155	2.994	4.161
M4	0.187	6.863	2.825	4.038
M3	0.227	7.059	2.947	4.112
M1	0.229	6.093	1.052	5.041
PNEA	0.261	5.452	2.166	3.286
PNMA	0.265	5.478	2.174	3.304
MENA	0.353	6.418	2.251	4.167
MNA	0.359	6.149	2.034	4.114
2-NDPA	0.364	5.973	2.521	3.452
M2	0.433	6.450	0.664	5.785
EC	0.444	6.062	0.597	5.465
2AMP	0.521	6.001	2.236	3.765
RES	0.548	6.034	0.142	5.891
C2	0.839	5.861	0.712	5.149

It can be seen from Tab. 3 that the EA and energy gap of MENA, MNA and EC are medium values. Although the EA value of PNEA and PNMA is also medium, it may not be easy to absorb free radicals because of its small energy gap. The new stabilizers M1-M5, M1 and M3 all have moderate EA, and the gap between HOMO and LUMO of M1 is also very large, which is easy to absorb nitrogen oxides.

3　Conclusion

Based on the above discussion, it can be conclu-

ded that among the 19 stabilizers，MNA，PNEA and EC have the strongest basicity. PNMA，RES and MNA have the strongest dissociation energy. PNMA and PNEA have larger NICS and better aromaticity. MENA，MNA and EC have better EA and energy gap. In summary，MNA，EC and RES can be selected as stabilizers in the propellants，which can absorb the oxides of nitrogen produced by the autocatalytic decomposition of nitrates and also have high stability. According to formula design of nitrate solid propellants，we can select good stabilizers which are compatible with propellant performance from the acid-base property，dissociation energy，aromatic property，electron affinity and energy gap of 19 stabilizers.

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