Green High Energy Density Material, N_2H_2O

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We proposed a new concept ''green high energy density material'' (HEDM) and designed some N_2H_2O isomers, i.e. oxadiaziridines (**1a**, **1b**), diimide *N*-oxides (**2a**, **2b**), hydroxydiimides (**4a**, **4b**) and nitrosoamide (**5**). These isomers satisfy the following conditions: (i) they have high energy densities; (ii) they have considerable kinetic stability; (iii) their green channels are favored more than non-green channels; and (iv) they have high possibility to be actually synthesized for practical use. The very high energy densities of oxadiaziridines (**1a**, **1b**) and the outstanding kinetic stability of diimide *N*-oxides (**2a**, **2b**) are strongly encouraging the first realization of green HEDM.

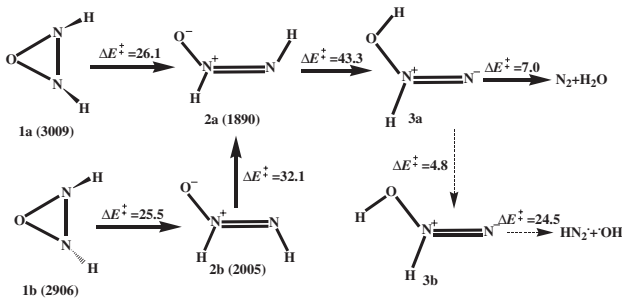
Recently, high energy density materials (HEDM) have received considerable attention as energetic carriers and fuels in various fields.[1] On the other hand, green chemistry is actively seeking ways to produce materials benign to human health and the environment.[2] Here, we report design of some ''green HEDMs'', i.e., oxadiaziridines (**1a**, **1b**), diimide *N*-oxides (**2a**, **2b**), hydroxydiimides (**4a**, **4b**) and nitrosoamide (**5**).

Our ''green HEDM'' should satisfy some criteria. First, it releases large heat on the decomposition. Second, HEDM should have good kinetic stability for actual use. Molecules usually have some channels for transformation with different activation energies. The lowest activation energy ($\Delta E_L^{\ddagger}$) of those of possible reactions is supposed to be higher than 25 kcal/mol. Third, the decomposition of the materials should produce the molecules (''green exhausts'') benign to human health and environments. We made the strictest choice for the products. The green exhausts should be the molecules, e.g., N_2, H_2O, etc. that exist in nature. It follows that the green channel should be more favorable than the non-green channels. Here, the green channel is defined as a sequence of reactions leading to the green exhausts, Finally, our HEDM should have high possibility to be actually synthesized for practical use.

Here, we designed some green HEDMs which produce N_2 or/and H_2O. The simplest candidates are N_4, H_4O_2, and N_2H_2O that may decompose to $2N_2$, $2H_2O$, or N_2+H_2O, respectively. The tetrahedral molecule N_4 has been extensively studied by quantum chemical theory.[3,4] However, the most serious problem for N_4 is the difficulty to find suitable precursors. Up to now, no species containing the N_4 unit have been synthesized. For the H_4O_2 system, it is difficult to imagine any isomers that possess high density and considerable kinetic stability. Therefore, we consider N_2H_2O. To our best knowledge, N_2H_2O has never been considered as a possible HEDM despite investigations on some N_2H_2O intermediates in the NH_2+NO reaction,[5] 1,3-dipolar properties,[6] and ring strain,[7] etc. Here, we will demonstrate that some N_2H_2O isomers are promising green HEDMs.

By exhaustive searching on the singlet potential energy surface, we locate 18 isomers and 47 transition states at the QCISD/6-31G(d) level followed by frequency calculations to confirm the nature of the 65 stationary points. The connection of each transition state is determined by intrinsic reaction coordinate (IRC) calculations at the B3LYP/6-31G(d) level using the B3LYP/6-31G(d)-optimized structures. The final energies of the QCISD/6-31G(d)-optimized isomers, transition states and fragments are refined at the Gaussian-3 level, which has been recently proposed and proved to be very accurate and effective.[8] All calculations are carried out using the Gaussian program package.[9]

The *cis*- and *trans*- isomers of the three-membered ring molecule (**1a** and **1b**) have the highest energy densities (3009 and 2906 cal/g)[10,12] with respect to the green exhausts N_2 and H_2O, respectively. Kinetically, **1a** and **1b** are significantly stabilized by the considerable barriers. The lowest activation energies $\Delta E_L^{\ddagger}$ are 26.1 and 25.5 kcal/mol for the ring opening reactions **1a**→**2a** and **1b**→**2b**, respectively. These values are large enough to allow the experimental characterization of **1a** and **1b**. Finally, the main green channels of **1a** and **1b** are indicated by the solid arrows in Scheme 1 ($\Delta E^{\ddagger}$ denotes the activation energy in kcal/mol and the values in parentheses are energy densities in cal/g). The most competitive non-green channel branches off at **3a**, as is indicated by the dotted arrows. The decomposition of **3a** to the final green exhausts is more favored than the isomerization of **3a** to **3b** followed by the decomposition to the non-green exhausts, HN_2 and OH radicals. The decomposition of **3a** to the green exhausts readily occurs because of the low activation energy (7.0 kcal/mol). The intermediates **3a** and **3b** undergo conformational change to each other with the low activation energy ($\Delta E^{\ddagger} = 4.8$ and 0.0 kcal/mol). The potential well for **3b** is very shallow (0.0 kcal/mol). The activation energy of the decomposition of **3b** to the non-green exhausts is higher (24.5 kcal/mol).



Scheme 1.

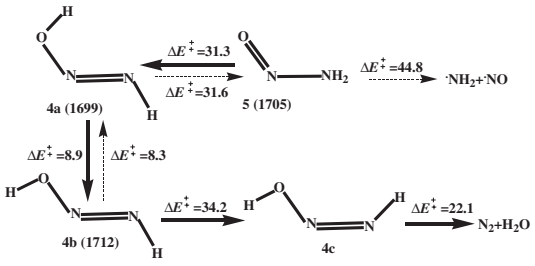
Although oxadiaziridines **1a** and **1b** have not been prepared yet, their alkyl (*i*-C_3H_7,[13] *tert*-C_4H_9, and *n*-C_4H_9[14,15]) derivatives were already experimentally known and were claimed to have ''surprising thermal stability''.[14] Interestingly, *trans*-oxadiaziridine **1a** was predicted[7] to have almost the same ring strain energy (27.1 kcal/mol) (despite the high energy) as cyclopropane (27.4 kcal/mol). The low ring strain makes the experimental

synthesis of oxadiaziridines promising. Oxadiaziridines (**1a** and **1b**) are expected to be powerful and promising "green HEDM". Further laboratory investigations are urged.

The *trans*- and *cis*-diimide *N*-oxides **2a** and **2b** have outstanding kinetic stability. Their $\Delta E_L^{\ddagger}$ values are 43.3 kcal/mol for **2a**→**3a** conversion and 32.1 kcal/mol for **2b**→**2a** conversion, respectively. Their energy densities are as high as 1890 and 2005 cal/g.[16] The main green channel and the most competitive non-green channel of **2a** and **2b** are the same as those of the latter parts of **1a** and **1b** (Scheme 1).

No synthetic reports for diimide *N*-oxides can be found in literatures. Yet, several previous reports on the preparation of the derivative substituted by i-C_3H_7,[13] *tert*-C_4H_9, and n-C_4H_9[17] groups suggest the possibility to be synthesized for actual use.

The energy densities (1699, 1712, and 1705 cal/g) of the *syn*- and *anti*-conformers **4a** and **4b** of hydroxydiimides and nitrosoamide **5** are also considerable.[18] The conformers of hydroxydiimides are separated by the very low energy barriers (ca. 8 kcal/mol). The kinetic stabilities of the isomeric mixtures **4a** and **4b** are considerable. The $\Delta E_L^{\ddagger}$ values are about 31 kcal/mol for the isomerization to nitrosoamide **5**. The kinetic stability of nitrosoamide **5** is also appreciable: $\Delta E_L^{\ddagger} = 31.3$ kcal/mol for the reverse reaction **5**→**4a**. Their main green and most competitive non-green channels are shown in Scheme 2. The isomers **4a**, **4b**, and **5** have very close energies. The critical step in the green channels is the isomerizaition of **4b** to **4c** with the barrier 34.2 kcal/mol. The critical step in the non-green channels is the decomposition of **5** to $HN_2^{\cdot} + {}^{\cdot}OH$ with higher barrier 44.8 kcal/mol (no transition state was located). The green channels are more favorable than the non-green channels by ca. 10 kcal/mol.



Scheme 2.

None of the hydroxydiimide isomers have been isolated or characterized. The substituted hydroxydiimides are formed by coupling aryldiazonium salts with hydroxide ion or alkoxides in the solution.[19] Nitrosoamide has been characterized by mass spectroscopy[20] and many of its substituted species are experimentally known.[19] Nitrosoamide is hopeful to be synthesized.

In summary, we have proposed a new concept "green HEDM" and designed seven N_2H_2O isomers (**1a**, **1b**, **2a**, **2b**, **4a**, **4b**, and **5**) as novel green HEDM candidates of high energy density, appreciable kinetic stability and the preference of the green channel to the non-green channels in the decomposition for the energy release. Some previous reports on the synthesis of the substituted N_2H_2O species strongly encourage the synthesis of these isomers. Particularly, oxadiaziridines (**1a**, **1b**) have very high energy densities and diimide *N*-oxides (**2a**, **2b**) have outstanding kinetic stability. The present work will open the way to science and technology of "green HEDM".

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