DFT INVESTIGATION OF STRUCTURES OF NITROSAMINE ISOMERS AND THEIR TRANSFORMATIONS IN GAS PHASE

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Abstract

The geometrical structures of H₂NNO nitrosamine isomers have been obtained by geometry optimizations using the DFT method at the RB3LYP/aug-cc-pVDZ level of theory. One amino, 4 imino tautomeris, 2 zwitertionic and 2 oxadiaziridine isomers of the H₂NNO nitrosamine have been found. The most stable species of the nitrosamine isomers existing as an amino form has been found. Energetics, thermodynamic properties, rate constants and equilibrium constants of all transformation reactions have been determined. The energy profile for the transformation reactions of the nitrosamine isomers has been presented.

Results and discussion

The structures of seven isomers of the H₂NNO nitrosamine and the transition states of all transformation reactions were obtained by geometry optimizations using DFT theory at the RB3LYP/aug-cc-pVDZ level of theory as shown in Fig. 1. The H₂NNO nitrosamine isomers can be classified into four types namely amino (type a), imino (type i), zwitertionic (type z) and oxadiaziridine (type o) isomers. Two zwitertionic forms which exist as the resonance structures are depicted as shown in Scheme 1.

The highest occupied molecular orbital (HOMO) and its five minimum orbitals (HOMO-1, HOMO-2, HOMO-3, HOMO-4 and HOMO-5) and transition states were confirmed by real and single imaginary vibrational frequencies, respectively. All reactions were optimized using density functional theory (DFT) method as shown in Fig. 2. The relative energies (ΔE) of the isomer z and z’ describe the occurrence of their delocalized structures which are displayed as shown in Scheme 1 and are possessed by four valence electrons of which energies are -8.0 eV. The HOMO and HOMO-1 orbitals of the isomer z and z’ describe the occurrence of their delocalized structures which are displayed as shown in Scheme 1 and are possessed by four valence electrons of which energies are -8.0 eV. The HOMO and HOMO-1 orbitals of the isomer z and z’ describe the occurrence of their delocalized structures which are displayed as shown in Scheme 1 and are possessed by four valence electrons of which energies are -8.0 eV.

The frontier molecular orbital energy gaps, ΔEHOMO-LUMO, are in kcal/mol.

Table 1 Rate constants of tautomerizations and isomerizations of all the nitrosamine isomers computed at the RB3LYP/aug-cc-pVDZ level of theory

Conclusions

The electronic properties of the amino nitrosamine isomers can be concluded as the following sequences.

1. Their relative stability is in the decreasing order: a > i > i’ > i” > z > z’ > o > o’.
2. Their relative reactivity based on their frontier molecular orbital energy gap is in the decreasing order: o’ > a > z > i’ > i > i” > o > z’.
3. Their acceptor strength is in the decreasing order: z > i’ > i > i” > o’ > o > z’.
4. Their donor strength is in the decreasing order: o’ > a > i > i” > i’ > o > z’.

References


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