Ab initio and quantum chemical topology studies on the isomerization of HONO to HNO_2. Effect of the basis set in QCT.

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Streszczenie

The article focus on the isomerization of nitrous acid HONO to hydrogen nitryl HNO(2). Density functional (B3LYP) and MP2 methods, and a wide variety of basis sets, have been chosen to investigate the mechanism of this reaction. The results clearly show that there are two possible paths: 1) Uncatalysed isomerisation, trans-HONO --> HNO(2), involving 1,2-hydrogen shift and characterized by a large energetic barrier 49.7 divided by 58.9 kcal/mol, 2) Catalysed double hydrogen transfer process, trans-HONO + cis-HONO --> HNO(2) + cis-HONO, which displays a significantly lower energetic barrier in a range of 11.6 divided by 18.9 kcal/mol. Topological analysis of the Electron Localization Function (ELF) shows that the hydrogen transfer for both studied reactions takes place through the formation of a 'dressed' proton along the reaction path. Use of a wide variety of basis sets demonstrates a clear basis set dependence on the ELF topology of HNO(2). Less saturated basis sets yield two lone pair basins, V(1)(N), V(2)(N), whereas more saturated ones (for example aug-cc-pVTZ and aug-cc-pVQZ) do not indicate a lone pair on the nitrogen atom. Topological analysis of the Electron Localizability Indication (ELI-D) at the CASSCF (12,10) confirms these findings, showing the existence of the lone pair basins but with decreasing populations as the basis set becomes more saturated (0.35e for the cc-pVDZ basis set to 0.06e for the aug-cc-pVTZ). This confirms that the choice of basis set not only can influence the value of the electron population at the particular atom, but can also lead to different ELF topology.

Słowa kluczowe

electron localization function, ELF, electron localibility indicator, ELI, topology, SAPT, hydrogen transfer, MP2, DFT, HNO2, HONO, nitrous acid, hydrogen nitryl, chemical bond