Electronic structure and the hydrogen-shift isomerization of hydrogen nitryl HNO$_2$

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Summary. Electronic structure of hydrogen nitryl HNO$_2$, a yet not identified entity, and the path of its possible isomerization to trans-HONO have been investigated by \textit{ab initio} SCF and MRD-CI computations using the 6-31G** basis set. HNO$_2$ is $C_2$-symmetric and its ground state ($^1A_1$) is less stable than trans-HONO by 66 kJ/mol (with the SCF vibrational zero-point energy correction). The lowest two excited singlet states ($^1A_2$ and $^1B_1$) are nearly degenerate, their vertical excitation energies being predicted to be 4.8 eV. The isomerization path is traced by the CASSCF procedure and the activation barrier height is evaluated by the CI treatment. HNO$_2$ in its ground state isomerizes to trans-HONO by maintaining the planar ($C_s$-symmetric) structure. The activation energy is calculated to be 171 kJ/mol, which is clearly lower than the calculated H–N bond energy (253 kJ/mol). The transition state seems to be more adequately described as an interacting system of proton and the nitrite anion rather than as a pair of two fragment radicals.

Key words: Hydrogen nitryl (HNO$_2$) – Nitro compound – Hydrogen migration – Isomerization

1 Introduction

In our previous work [1], we investigated the gas-phase reaction of NH with O$_2$ by the \textit{ab initio} method. It was found that the reaction between NH($^3\Sigma^-$) and O$_2$($^3\Sigma_g^-$) should proceed by an initial association giving a chain intermediate HNOO($^1A'$):

\[
\text{NH}(^3\Sigma^-) + \text{O}_2(^3\Sigma_g^-) \rightarrow \text{HNOO}
\]  

(1)

By contrast, the reaction between NH($^1A$) and O$_2$($^1A_g$) should be a concerted cycloaddition to give a cyclic HNO$_2$. It will easily isomerize into nitrous acid.
HONO via an acyclic HNO$_2$ (I) of the $C_{2v}$ symmetry [2]:

$$\text{NH}(^1A) + \text{O}_2(^1A_g) \rightarrow \text{H-N-O} \rightarrow \text{H-N-O}$$ (2)

$$1 \rightarrow \text{HONO}$$ (3)

The singlet species 1, which we here refer to as hydrogen nitryl, is the branched isomer of nitrous acid 2 and should be the simplest possible nitro compound. It has never been identified experimentally so far. The challenge to identify this isomer was first made by Jones et al. [3], who observed no indication of its contribution in the IR spectra of gaseous nitrous acid. It could also be one of the transient intermediates of the well-known gas-phase reaction of the H atom with NO$_2$ to produce the NO and OH radicals [4–8]. Guillory et al. [9] carried out IR spectroscopic studies of the products of the H + NO$_2$ reaction conducted by the matrix isolation technique, to observe cis- and trans-HONO alone; no trace of the nitro form (1) was discernible.

Hydrogen nitryl (1) may be used as a convenient prototype for existing nitro compounds in assessing their thermochemical stabilities relative to the chain isomers [10]. To the best of our knowledge, however, there has been no explicit study to trace the path of its isomerization pathway (Eq. (3)). Elucidation of the intrinsic path of Eq. (3) by \textit{ab initio} SCF and CI calculations is the primary concern of the present investigation. We will also attempt theoretical predictions of the vertical singlet excitation energies of 1.

2 Method of calculations

The path of isomerization was traced first by the RHF SCF procedure, using the Gaussian 86 program package [11]. The atomic orbital functions used in this study are primarily the 6-31G** basis set [12] throughout, unless otherwise stated. The transition state (TS) was located and verified by the vibrational analysis. For all the stationary points on the isomerization path (i.e., HNO$_2$, TS, and \textit{trans}-HONO), CASSCF (8 electrons in 6 orbitals) calculations by the use of the HONDO program [13] were then performed to improve their geometries. For the fragment radicals, the unrestricted Hartree-Fock (UHF) method was used.

At all the optimized geometries, multi-reference double-excitation configuration-interaction (MRD-CI) calculations were carried out. The Table CI program [14, 15] furnished by Buenker was used. The configuration-selection and extrapolation routines were followed [16]. The maximal dimension of the configuration space used was 8000–10,000. The extrapolated CI energies were all subjected to the Langhoff-Davidson corrections [17], to estimate the full CI limit values $E_{\text{CI}}$. To determine the reference (main) configurations, we preliminarily performed a single-reference SD-CI calculation at each state. The configurations whose contributions $|C_i|^2$ to a state under consideration exceeded 0.3% were then regarded as the reference configurations. In this manner, the total number of the reference configurations adopted were typically 3 to 5, and the total sum of the weights $|C_i|^2$ of the reference configurations were at least 0.90.