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Theoretical study of water reaction in the N-Hydroxy-Methylen-Formamide

Anoop Kumar
M.Sc. Chemistry, CH. Dadri, Haryana, India

Abstract
The present work deals with the study of proton transfer in the isolated, mono and dehydrated forms, isolated dimers of N-Hydroxy Methylen Formamide (NHMF). The Density Functional The-ory (DFT), Möller-Plesset perturbation (MP2) and Hartree-Fock (HF) methods with the 6-31G* and 6-311G* basis sets also have been discussed in the paper. The barrier heights for both H_2O-assisted and auto-assistance reactions are significantly lower than that of the bare tautomerization reaction from NHMF to N-Formyl Formamide (NFF).

Keywords: N-Hydroxy Methylen Formamide, MP2 and DFT

1. Introduction

The NHMF (Figure 1) [1] is the smallest N-acyled Imidate which contains the two amide and oximin forms of the formamide tauto-meric equilibrium.The internal coordinates optimization of the different conformers: trans-trans, cis-cis and trans-cis lead to stables structures, respectively, of the same configuration that the initial input and no imaginary frequencies were found. The cis-trans optimization leads to a transition state. The cis-cis structure is stabilized by intra-molecular hydrogen bond between H_8 and O_4. The lengths of the links C=N and C= O, in the trans-cis conformer, correspond in all cases to the localized links by comparing them to the experimental data that we met for C=N in the conjugated imines [2] and the C=O in the formamide’s family [3, 4].

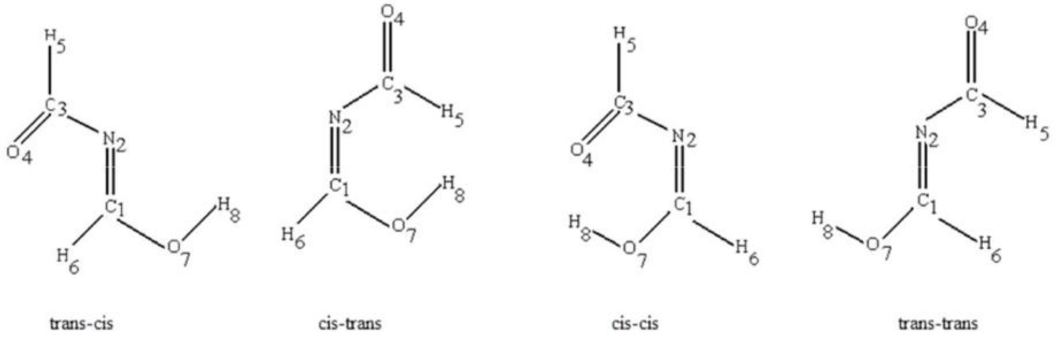

Fig 1: Different structures of the N-Hydroxy Methylen Formamide (NHMF) [1].

The conformational energy reaction cis-cis to trans-cis is endothermic of 4.29 kcal/mol at B3LYP/6-31G* level. The change of configuration passes by a transition state which is situated at an energy barrier of 26.20 kcal/mol at HF/6-31G* and 30.65 kcal/mol at B3LYP/6-31G* level [1]. These activation energies are high enough to allow, in warm conditions, the passage from one to the other of the two conformers. Thus, the two structures cis-cis and trans-cis exist; the first one in the absence of the other. The calculation of the electronic energy, corrected energy at the zero point and thermal energy, leads for HF, MP2 and B3LYP/6-31G* to the same order of stability:

Cis-cis > trans-cis > trans-trans > cis-trans.

In one hand the trans-cis form becomes strongly pre-dominant in the polar solvent because of its high dipole moment, which is much greater than that of cis-cis forms and on the another hand, these two forms in the cis-cis tautomeric equilibrium are identical. All these facts explain our choice of the equilibrium tautomer study of the trans-cisforms of the NHMF molecule which contain in the same time the amide and imidic forms of the formamide molecules. The formamide-formamidic tautomerization has been used to a model in large basic linkage in peptides and proteins. Several theoretical studies on the monohydrated (bi-hydrated) formamide-water complex have deter-mined that the preferred mechanism for proton transfer to form formamidic acid proceeds via stable cyclic dou-ble or triple hydrogen bonded transition state [6-11]. The energy barrier for the formamide→formamidic acid isomerization was estimated by Wang *et al.* [8] to be 48.9 kcal/mol in the gas phase. But in the same article it was shown that a single H_2O molecule directly assists the tautomerization of formamide lowers the barrier to 22.6 kcal/mol.

2. Computational Methods

In this work, all computations were carried out by means of the Gaussian 03W [12]. All the geometries of local minima and transition state structures were optimized without symmetry restrictions (C1 symmetry was as-sumed) by the gradient procedure initially at the HF level and subsequently at the second order of closed shell Möller-Plesset perturbation theory [13]. The results have been compared with those obtained from the Functional Density Theory (DFT) by using the function of exact exchange of Becke (B3) [14] and the function of the gradient correction of Lee Yang Parr (LYP) [15].

3. Results and Discussion

The structures and frequencies of the equilibrium ge-ometry were discussed briefly in the introduction of this work and in detail by Brahimi *et al.* at the HF, post-HF (MP2) and density functional theory levels for the iso-lated NHMF [1].

Self, Water-Assisted and Self-assisted Proton Transfer Reaction in the NHMF Molecules

Geometries

The self -proton transfer from O $_7$-H$_8$ to N$_2$ in the NHMF gives the N-Formyl Formamide (NFF) molecules. Figure 2 shows the geometries of the reactants, transition states and products involved in the self, H_2Oassisted, $(H_2O)_2$-assisted and self-assisted NHMF proton transfer reac-tions obtained at HF, MP2 and DFT/B3LYP levels with 6-311G* basis. For the self mechanism (NHMF TS NFF), the transi-tion state appears to hold a co-planar four-membered-ring. When we exam the structural changes from reactant to product, it can be seen that the C=N-C=O dihedral angle fluctuate according to the theoretical level used, this angle worth 0.0(9.4) at the HF, 28.2(32.7) at the MP2 and 23.8(27.9) degrees at the B3LYP//6-31G* (6-311G*), and the C=O bond length does not vary from reactant to product via transition state.

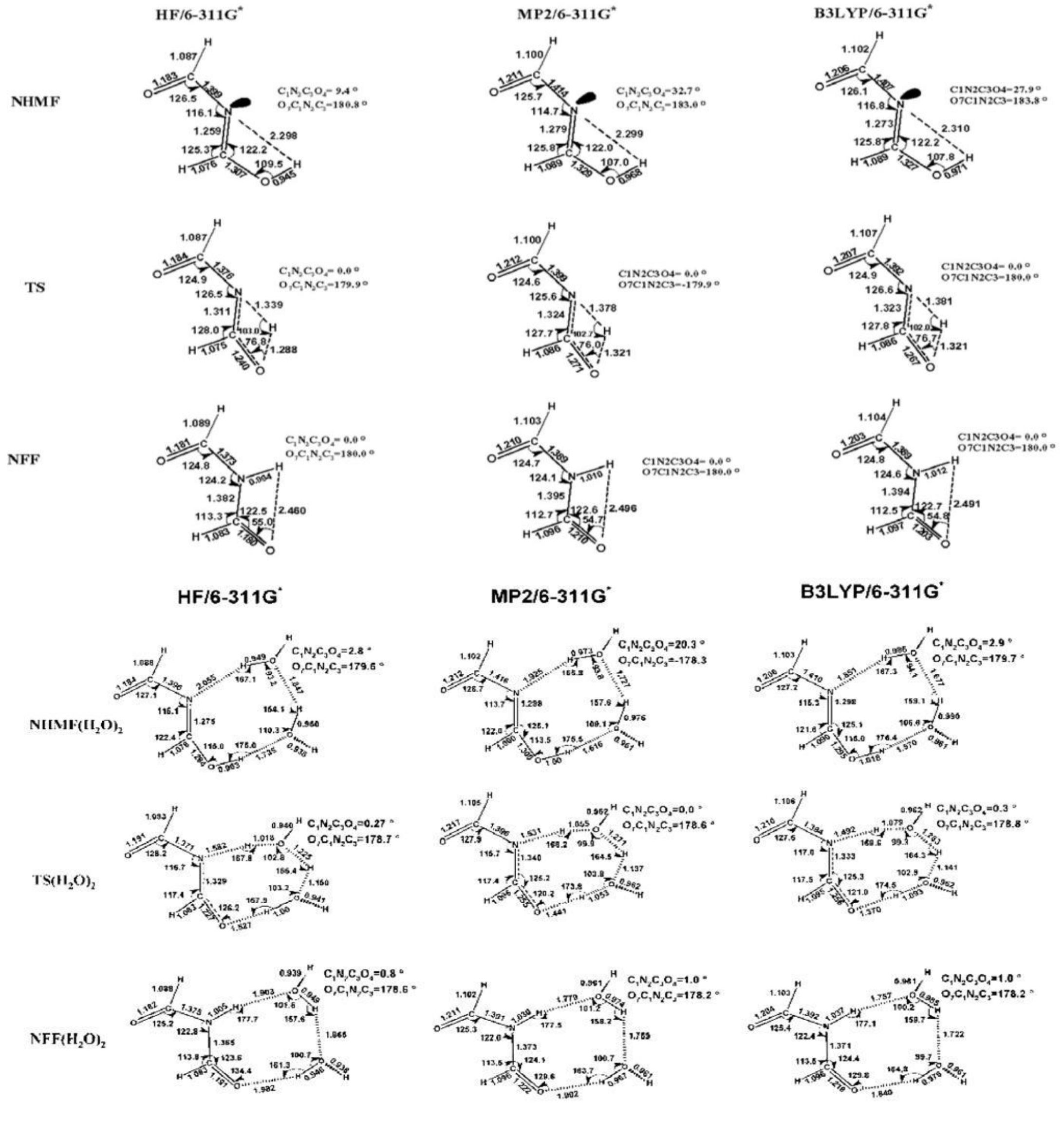

Fig 2: The optimized structures of the reactants, transition states and products of the (a) Self, (b) H_2O-assisted, (c) $(H_2O)_2$-assisted and (d) auto-assisted tautomeric process.

For H_2O-assisted tautomerization (NHMF(H_2O)→ TS(H_2O)→FF(H_2O)), the most stable geometry of reac-tant NHMF(H_2O) is the cyclic double-hydrogen bonded structure. The two hydrogen bonding distances are 2.205 (2.253) Å and 1.833 (1.814) Å, respectively, at HF//6-31G* (6-311G*) levels. These results are in good agreement with those obtained by Ai-Ping-Fu and Col. in the study of proton transfer in the formamide [11]. In the NFF(H_2O) product, it is also a double hydrogen bonded system with the two hydrogen bonds and are 2.044 (2.014) Å and 2.132 (2.168) Å, respectively, at HF/6-31G*(6-311G*) level. In comparison with the self-tautomerization, the obvious difference is that the N_2C1O_7 angle has to be compressed by only 1.2 degrees at MP2/6-311G* level (for NHMF→NFF is 13.3˚). The passage of isolated NHMF tautomeric form to the hy-drated ones leads a net variation of the $C_1N_2C_3O_4$ dihe-dral angle. On DFT/B3LYP level, its value (23.8 without H_2O) becomes (4.7 with H_2O) degrees with 6-31G* basis and (27.9) becomes 11.3 degrees with 6-311G* basis. On MP2 level, its value passes from 28.2 to 12.6 degrees with 6-31G* basis and from 32.7 to 21.2 degrees with 6-311G* basis. On HF level, its value passes from 0 to 2.8 degrees with 6-31G* basis and from 9.4 to 2.9 degrees with 6-311G* basis. Thus, the introduction of one water molecule has an effect on the planarity of the system but not the delocalization for the π electrons. In fact, the C_1=N_2 and C_3=O_4 bonds correspond, in all cases, to a localized bonds. In the NFF structure, the solvent effect is practically vanished. For the NHMF self-assisted mechanism, the optimized geometries of the stationary points, transition state at HF, MP2 and DFT/B3LYP levels with 6-311G* are also il-lustrated in Figure 2 being similar to the water-catalyzed reactions, the reactant of the NHMF dimer also forms a co-planar eight membered-ring via two equivalent hydrogen bonding. The hydrogen bond distance is 1.872 and 1.629 Å, respectively at HF and B3LYP//6- 311G* level. Similarly, NFF dimmer also appears to be a cyclic double hydrogen bonded structure with the hydrogen bond distance is 2.006 and 1.889 Å, respectively at HF and B3LYP//6-311G * level. In NHMFdimer, the NHO angle is quasi-linear (179.9 at B3LYP//6-311G* level) causing the proton easier to transfer from the oxygen atoms towards the nitrogen ones. In all cases, the two forms NHMF-dimmer and NFF-dimer exhibit a plan structures.

Energetic

Figure 3 explains the reactants, transition states and products involved in the 1) self, 2) H_2O-assisted, 3) $(H_2O)_2$-assisted and 4) self assisted NHMF proton transfer reactions obtained at HF, MP2 and DFT/B3LYP levels with 6-311G* basis.

It appears that the NHMF→NFF energy reaction, with ZPE correction, is exothermic of 17.35, 17.61 and 17.17 kcal/mol. at the HF, MP2 and DFT/B3LYP//6- 311G* level, respectively, thus the NFF form is the most stable than that NHMF one. In one hand, Figure 3 shows that the NHMF (H_2O)→ NFF(H $_2$O) is also exothermic. We note that the two NHMF and NFF hydrated molecules are slightly stabilized comparing to the isolated molecules. The energetic gap from the two reactions, hydrated and isolated, is reduced by 1.32(1.47), 1.12(1.27) and 3.25(3.23) kcal/mol. at the HF, MP2 and DFT/B3LYP//6-31G* (6-311G*) level, respectively. We note also that the solvent effect decrease the barrier of the activation energy. The gap energy is 23.13(24.30), 22.37(23.83) and 8.80(10.15) kcal/mol. at the HF, MP2 and DFT/B3LYP//6-31G*(6-311G*) level.

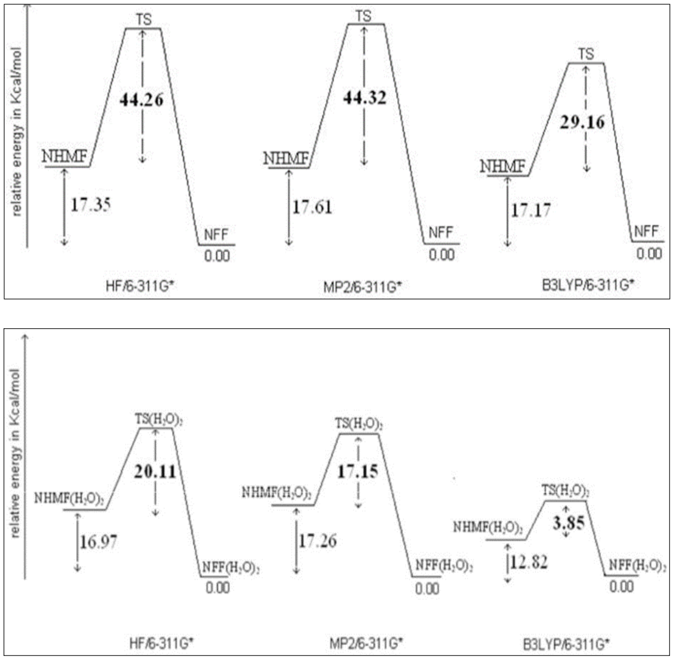

Fig 3: The optimized structures of the reactants, transition states and products of the (a) Self, (b) H_2 O-assisted, (c) $(H_2O)_2$-assisted and (d) auto-assisted tautomeric process

In another hand, the results, obtained at the different level of theory (with ZPE correction), show that the NHMF $(H_2O)_2$→NFF$(H_2O)_2$ is exothermic by 16.97, 17.26 and 12.82 kcal/mol at the HF, MP2 and B3LYP//6-311G* level, respectively. These energies barriers are the same with those obtained for the NHMF (H_2O)→NFF(H_2O) reaction for the proton transfer when we use one water molecule. The DFT/B3LYP level, conduce to the small-est energy barrier, see 3.85 kcal/mol. This proves that the second water molecule addition doesn't have an effect on all the different energetic value.

4. Conclusions

All theoretical levels, in aqueous environments, tend to decrease the energy barrier and the energy tautomeri-zation compared to the gas phases. The HF and MP2 results promote the existence of the two NHMF and NFF separate molecules in the gas phase and hydrated ones. DFT leads a lower barrier energy compared with those obtained at the HF and MP2 levels. Thus this method provides the simultaneous existence of the both molecules in the both environments. Finally, the NHMF→NFF reaction is established on a self-assisted NHMF dimmer with low barrier energies

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