S_N2-like Reaction in Hydrogen-Bonded Complexes: A Theoretical Study

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S_N2-like reactions in hydrogen-bonded complexes have been investigated in this paper at a correlated MP2-(full)/6-311++G(3df,3pd) level, employing FH···NH_3···HF and ClH···NH_3···HCl as model systems. The unconventional F(Cl)−H···N noncovalent bond and the conventional F(Cl)−H···N hydrogen bond can coexist in one complex which is taken as the reactant of the S_N2-like reaction. The S_N2-like reaction occurs along with the inversion of NH_3 and the interconversion of the unconventional F(Cl)−H···N noncovalent bond and the conventional F(Cl)−H···N hydrogen bond. In comparison with that of the isolated NH_3, the inversion barriers of the two complexes both are significantly reduced. The effect of carbon nanotube confinement on the inversion barrier is also discussed.

Introduction

In a previous study, we reported a new type of unconventional intramolecular and intermolecular interactions in N(P)-containing systems in which the X−H bond attacks the electronegative N(P) atom from the backside of its lone electron pair.[1] This type of interaction has common features of a hydrogen bond, while deviation from Popelier's eight criteria[2,3] for a hydrogen bond was also found according to a comparative analysis of electron density topology.[1] It is well-known that the traditional hydrogen bond forms when the X−H bond approaches the electronegative N(P) atom from the front side of its lone electron pair.[4] Then, a natural question is: Can the rear-face attack and the front-face attack coexist? In other words, does there exist any complex which, as well as including the traditional hydrogen bond formed at the front side of the lone electron pair on N(P) atom, also includes the unconventional noncovalent bond formed at the backside of the same lone electron pair simultaneously? Furthermore, if there exist such complexes, can S_N2-like reaction happen in these complexes? As illustrated in Figure 1, if such a S_N2-like reaction occurs, one monomer enters as the other monomer leaves, attacking the N(P) atom from the side opposite to that from which the other monomer departs. This results in the formation of a new hydrogen bond and the disruption of the old hydrogen bond. At the same time, the proton acceptor at the reaction center undergoes an "umbrella" inversion when the reaction occurs. Therefore, strictly speaking, this S_N2-like reaction is a hydrogen bond assisted inversion reaction. To answer these questions, in this paper, we report the second-order Møller−Plesset theory based (MP2-based) quantum chemical studies on two model complexes FH···NH_3···HF and ClH···NH_3···HCl. It should be pointed out that the complexes selected in this paper are simple but representative and this kind of S_N2-like reaction may also happen in other N(P)-containing complexes.

Computational Details

Using the Gaussian 03 suite of programs,[5] structures were optimized and characterized by frequency computations at the MP2(full)/6-311++G(3df,3pd) theory level. Intrinsic reaction coordinate (IRC) calculations[6] were also used to verify the identity of the transition structure associated with the interconversion of reactant and product (see Supporting Information). The basis set superposition error (BSSE) was eliminated by the standard counterpoise (CP) correction method of Boys and Bernardi.[7] To explore the effect of confinement of a S_N2-like reaction system inside a carbon nanotube, single-point calculations were carried out using the isodensity polarizable continuum model (IPCM).[8]

The bonding characteristics of the different systems were analyzed by using the "atoms in molecules" (AIM) theory of Bader,[9] which is based on a topological analysis of the electron charge density and its Laplacian. The analysis went further with those obtained by means of the natural bond obital (NBO) theory of Weihnhold and co-workers.[10] AIM analysis was carried out employing the AIM2000 code[11] with the MP2 wave functions as input. NBO analysis used the MP2-optimized structures, the Hartree−Fock (HF) densities, and the built-in subroutines of the Gaussian 03 program.

The performance of the all-electron MP2 method with the 6-311++G(3df,3pd) basis set is examined by studying three small monomer molecules. The optimal bond lengths of HF and HCl calculated at the MP2(full)/6-311++G(3df,3pd) level are 0.9156 and 1.2683 Å, respectively, which is in very good agreement with experimental values of 0.9169 and 1.2746 Å.[12] For ammonia, the MP2(full)/6-311++G(3df,3pd) bond length of 1.0109 Å and bond angle of 106.9° also compare well with the experimental bond length of 1.0120 Å and bond angle of 106.7°.[12] The calculated inversion barrier of NH_3 of 4.80 kcal/mol should be comparable with the literature value of 5.05 kcal/mol.[13−15]

Results and Discussion

The optimized geometries for reactants, transition states, and products of two studied complexes are illustrated in Figure 2, along with some salient geometrical parameters and inversion barriers. The corresponding molecular graphs are shown in Figure 3. Figure 3 also contains the results of a NBO analysis. For comparison, we also presented the related results of NH_3.

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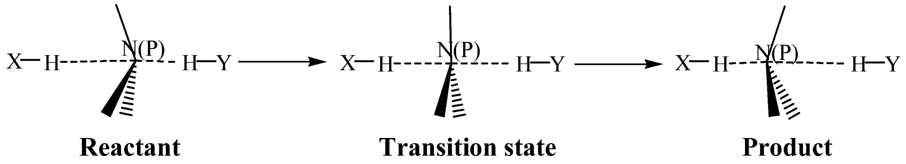

Figure 1. S_N2-like reaction in N(P)-containing complexes. The dashed lines represent noncovalent bonds.

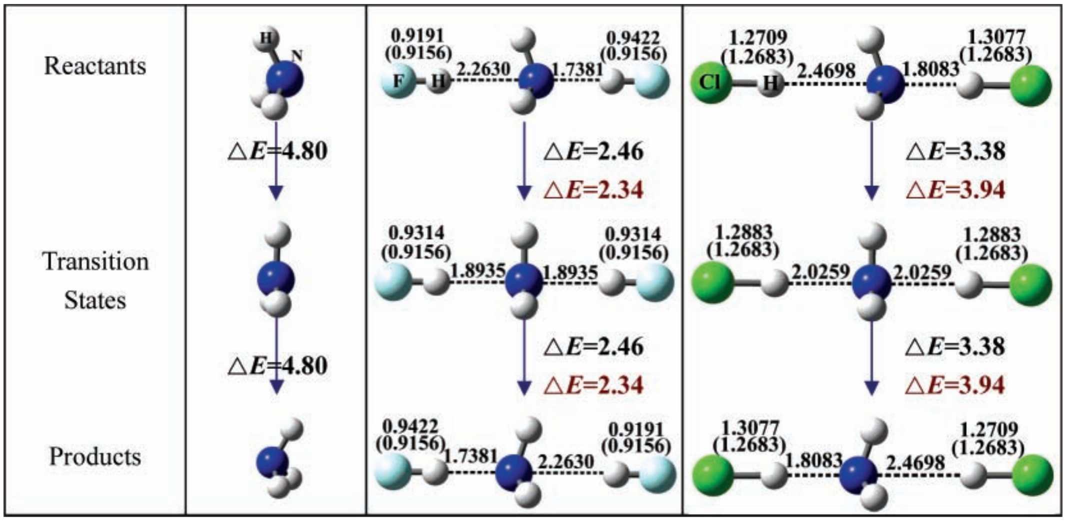

Figure 2. Optimized geometries and inversion barriers for the reactants, transition states, and products of NH_3, FH···NH_3···HF, and ClH···NH_3···HCl, respectively. Bond lengths are reported in angstroms and inversion barriers (ΔE) in kilocalories per mole. In parentheses are the bond lengths corresponding to the monomers. Inversion barriers inside the (8,0) or (9,0) carbon nanotube are shown by magenta numbers. The dashed lines represent noncovalent bonds.

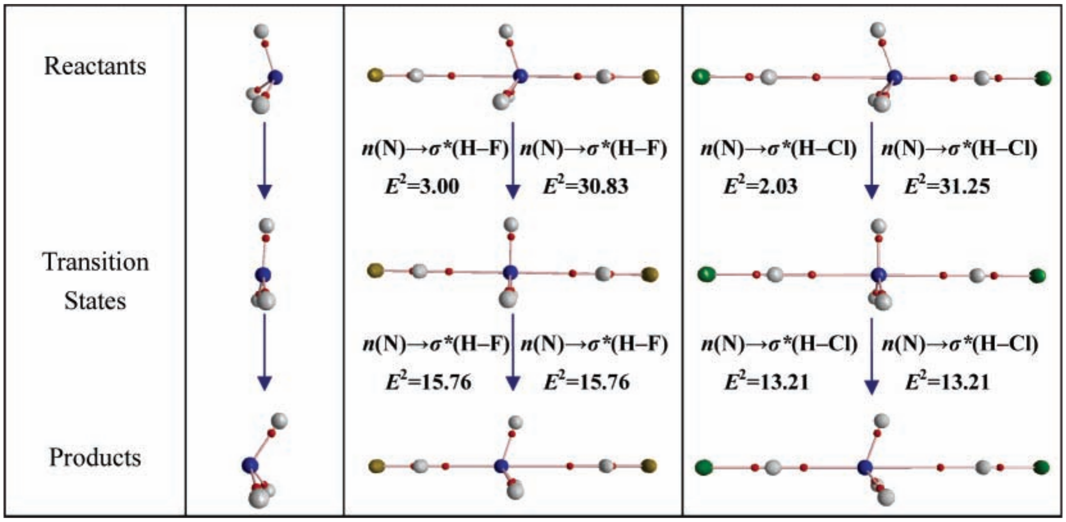

Figure 3. Molecular graphs for the reactants, transition states, and products, together with some significant donor−acceptor orbital interactions and their second-order perturbation stabilization energies (E^2, kcal/mol). Bond critical points are denoted by red dots.

From Figure 2, it can be clearly seen that the unconventional noncovalent bond and the hydrogen bond can coexist in the reactant or the product of one complex. They both transform into new hydrogen bonds in the transition states of the two complexes. The molecular graphs in Figure 3 confirm this again. Note that the AIM theory has proved itself a valuable tool for conceptually defining what is an atom and above all what is a bond in a quantum calculation of a molecular structure.[9] As shown in Figure 2, the H···N distances within the unconventional noncovalent bonds are all longer than H···N distances within the hydrogen bonds. The relatively strong character of the hydrogen bond is associated with a high degree of electron transfer from the nitrogen lone pair to the antibonding orbital σ^*(H−F(Cl)), as is evident in Figure 3. In the reactant or the product of the FH···NH_3···HF complex, the elongation of the F−H bond length within the unconventional noncovalent bond is 0.0035 Å upon complex formation, which is shorter than the elongation of 0.0266 Å within the hydrogen bond. The ratio of the two values is about 1:8. Corresponding to the change of the F−H bond length, the second-order perturbation stabilization energy (E^2) due to the interaction of donor (n(N)) and acceptor (σ^*(H−F)) orbitals is 3.00 kcal/mol for the unconventional noncovalent bond and 30.83 kcal/mol for the hydrogen bond. Their ratio is roughly 1:10, which is close to the ratio of the F−H bond elongation. For the reactant or the product of the ClH···NH_3···HCl complex, the ratio of the Cl−H bond elongation (0.0026:0.0394 = 1:15) is almost equal to the ratio of the second-order perturbation stabilization energy (2.03:31.25 = 1:15). The transition structures of the two complexes are highly symmetrical, so the structures or properties of the two hydrogen bonds in each complex are one and the same. A first conclusion from the above analysis is that the change of the F(Cl)−H bond length is mainly derived from a significant charge transfer from the lone pair of the nitrogen atom to the antibonding orbital σ*(H−F(Cl)). The second conclusion is that, in order for the S_N2-like reaction to occur, the antibonding orbital of the proton donor at the backside of the nitrogen lone pair should have a strong capability to accept electron density. The stronger the antibonding orbital to accept electron density, the easier the S_N2-like reaction is to occur.

The inversion barriers in Figure 2 are 2.46 kcal/mol for the complex FH···NH_3···HF and 3.38 kcal/mol for the complex ClH···NH_3···HCl. Both are smaller than the inversion barrier of NH_3 of 4.80 kcal/mol. The explanation for the smaller inversion barrier of NH_3 in the NH_3-containing complexes is that the formation of the strong hydrogen bond stabilizes the transition state. The BSSE-corrected interaction energies for the reactant and transition state of the complex FH···NH_3···HF are 11.98 and 13.52 kcal/mol, respectively. These values become 8.38 and 9.09 kcal/mol, respectively, for the reactant and transition state of the complex ClH···NH_3···HCl. Obviously, the BSSE-corrected interaction energies of the transition states are both larger than those of the reactants. So, the inversion barrier of NH_3 in the complex is smaller than that of the isolated NH_3. The difference of the BSSE-corrected interaction energies between the reactant and the transition state of the complex FH···NH_3···HF is 1.54 kcal/mol, larger than 0.71 kcal/mol of the complex ClH···NH_3···HCl, which results in the smaller inversion barrier of NH_3 in the complex FH···NH_3···HF than in the complex ClH···NH_3···HCl.

Halls and Schlegel explored the Menshutkin S_N2 reaction inside (8,0) and (9,0) carbon nanotubes.[16] They found that the activation energy and reaction endothermicity for the Menshutkin S_N2 reaction are significantly reduced compared to those in the gas phase and the effect of carbon nanotube confinement on reaction enthalpies closely resembles solvation in a low-dielectric solvent. In the present study, the effects of confining two S_N2-like reactions inside (8,0) and (9,0) carbon nanotubes on inversion barriers are also investigated. Calculations are carried out employing an isodensity polarizable continuum model to represent the effects of nanotube confinement. The effective dielectric constants for inversion processes inside the (8,0) and (9,0) carbon nanotubes are 2.876 and 2.410.[16] The results are shown in Figure 2 in magenta numbers. According to our calculations, the inversion barriers inside the (8,0) carbon nanotube are the same as those in the (9,0) carbon nanotube. In comparison with the inversion barrier in the gas phase, the carbon nanotube confined inversion barrier decreases 0.12 kcal/mol for the complex FH···NH_3···HF and increases 0.56 kcal/mol for the complex ClH···NH_3···HCl. The effect of carbon nanotube confinement on the inversion barrier is not very meaningful, which is totally different from the case of the Menshutkin S_N2 reaction. This is understandable because no charged species are involved in the whole reaction process. Therefore, the S_N2-like reaction studied here may not be enhanced inside fullerene-based materials.

In summary, we have theoretically described a new type of S_N2-like reaction in the NH_3-containing complexes. While exotic in their appearance, such reactions might occur in true biological systems because amido groups are the most common sites for molecular recognition through hydrogen bonding in natural systems on one hand and the inversion barriers are low on the other hand. Furthermore, they may even have a role in determining the structures and functions of some biologically important macromolecules. Both of these possibilities are under investigation in our laboratories.

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Supporting Information Available: IRC calculations for two S_N2-like reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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