Bonding Rearrangements of Hydrogen-Bonded Complexes Involving Alkynes

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Molecules containing a C−C triple bond, such as HC≡CH, FC≡CF, and the C≡CH radical, are allowed to interact with a partner molecule of H_2O, NH_3, or HF. Quantum chemical calculations show that these C≡CH···X H-bonded complexes are bound by up to 4 kcal·mol^{-1}. More importantly, they can rearrange in such a way that the partner molecule adds to the triple bond so as to form a double C═C bond. Whereas this process is strongly exoergic, there is a high-energy barrier to this rearrangement process. On the other hand, when a second water molecule is added to the complex, it can shuttle protons from the donor part of the complex to the acceptor, and thereby greatly reduce the rearrangement energy barrier. In the case of CCH + $2H_2O$, this barrier is computed to be less than 4 kcal·mol^{-1}.

Introduction

The first, doorway step in a bimolecular process is frequently the association of a pair of molecules in some sort of weakly bound dimer, as they approach one another from infinity. The interaction might take the form of a weak van der Waals complex or could be something a little stronger as in the hydrogen bond between a pair of water molecules, or even a tightly bound ion pair. In many cases, this dimerization represents a “dead end” in the reaction as it is the most stable accessible arrangement of the atoms involved, which is the case for a large number of hydrogen-bonded complexes.[1−4] In other situations, however, the complex can undergo a rearrangement to a more stable entity. A typical example might be the proton transfer from one subunit to another that follows after the formation of the initial H-bonded complex.[5−11] This transfer is not limited to ground states but can occur in an excited electronic state as well.[12−17] Another sort of process[18] begins with a system held together initially by a dihydrogen (H··H) bond, followed by rearrangement to a dihydride. In the latter cases where the interaction is a prelude to a second process, the dimer is characterized by a finite lifetime, often sufficiently long to observe this dimer, which can be categorized as a sort of metastability.

H-bonded complexes most commonly fall in the former category, quite stable, more prone to a dissociation to the original reactants than to any sort of rearrangement process. The water dimer serves as an example, in that the rearrangement of $(H_2O)_2$ to some other, more stable entity, would not seem likely or even possible. In contrast, there are other H-bonded complexes where a particular sort of rearrangement might be anticipated to lead to something more stable than the originally associated pair of molecules. For example, alkenes and alkynes contain double and triple C−C bonds, respectively. Considering acetylene as an example, although a water molecule would be expected to first form a H-bonded HC≡CH···OH_2 complex, the water molecule could dissociate internally and thereby convert the alkyne to a H_2C═CHOH alkene molecule. On the other hand, even if the final product is considerably more stable than the initial complex, the transformation would likely need to traverse an energy barrier. A high barrier would make this process untenable, on a time scale making it immeasurable, but a lower barrier would permit this combination reaction to occur. In such a case, the H-bonded complex could be considered a metastable reaction intermediate, or alternately as an isomer that might be kinetically stable if the barrier confers a sufficiently long, but finite, lifetime.

The purpose of the present work is an examination of triply bonded alkynes, and their complexes with small solvent molecules such as H_2O and NH_3 and HF. The rearrangement process that would follow the dimerization is examined in some detail, with particular attention paid to the energetics of the process and the reaction trajectory. This information will help to deduce whether the H-bonded complexes are thermodynamically and/or kinetically stable, or might be better thought of as reaction intermediates along a rearrangement pathway. Another issue addressed concerns the potential catalytic activity of a second solvent molecule. Numerous prior studies have shown that a proton transfer from one part of a molecule to another can be strongly facilitated by the presence of a solvent molecule such as water. The latter acts as a sort of relay, accepting a proton from one part of the molecule, and delivering another proton to the acceptor segment of the molecule. We consider here whether such a mechanism can be active in the alkyne rearrangement process under study.

Computational Methodology

All calculations were performed by the second-order perturbation Møller−Plesset frozen-core method (MP2) or hybrid density functional B3LYP technique using the *GAUSSIAN 03* suite of programs.[19a] Various basis sets, denoted as B_1 = 6-311+G(3df,2p), B_2 = 6-311++G(3df,2pd), B_3 = 6-311+G(2df,2p), and B_4 = 6-311++G(3df,2p) were applied. All geometry optimizations were carried out with the TIGHT option. MP2 and B3LYP harmonic vibrational frequencies were cal-

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TABLE 1: Properties of the Studied H-Bonded Complexes

A	B	H-bond type	E_{HB},[i] kcal·mol^{-1}	R(H···X), Å	Δr(YH), Å	$\Delta\nu$(YH), cm^{-1}
HCCH	NH_3	CH···N	3.1; 1.9[a,g]	2.307	0.010	−108
			3.8; 2.6[b]	2.279	0.009	−102
HCCH	OH_2	CH···O	2.5; 0.4[c]	2.227	0.006	−53
			3.1; 1.0[f]	2.187	0.005	−47[h]
HCCH	FH	CH···F	1.4;[a] <0	2.294[a]	−0.002	−17
			1.9;[e] <0	2.236[e]	−0.001	−12
HCC	OH_2	CH···O	3.1[a]	2.162	0.001	−40
FCCF	OH_2	OH···π	0.6; −0.5[d]	2.635	0.001	−22
			1.4; 0.1[b]	2.505	0.001	−18
HCCH	$2OH_2$[c]	CH···O	7.0[c]	2.251	0.002	−17
		OH···π		2.408 (H···C)	0.003	−38
FCCF	$2OH_2$[c]	OH···π	4.9[c]	2.600 (H···C)	0.001	−17
HCC	$2OH_2$[d]	CH···O	5.0[d]	2.123	0.006	−125
		OH···π		2.588 (H···C)	0.006	−67

[a] B3LYP/B_1. [b] MP2/B_1. [c] B3LYP/B_4. [d] B3LYP/B_2. [e] MP2/B_3. [f] MP2/B_4. [g] The BSSE-corrected binding energy amounts to 3.0 kcal·mol^{-1} at the B3LYP/B_1 computational level.[20] The BSSE corrections for the first three systems were estimated in Table 2 of ref 20b and ranged within the interval 0.3−0.5 kcal·mol^{-1}. [h] The harmonic frequency red shift $\Delta\nu_{asym}$(C−H) = −40 cm^{-1} was estimated at the MP2/aug-cc-pVTZ computational level in ref 22k. The experimental values are reported as 63 and 34 cm^{-1} in the Ar matrices[22i] and in a nozzle expansion of a mixture of acetylene in He and water.[22e] [i] Left and right entries correspond respectively to ZPE-uncorrected and corrected values. E_{HB} refers to ΔE for complexation.

TABLE 2: Energetics of Rearrangement Process (kcal·mol^{-1}) Wherein A and B Represent Reactants

A	B	product	ΔE[f]	ΔH[i]	$E^{\dagger}$,[g]	$\Delta H^{\dagger}$,[i]
HCCH	NH_3	$NH_2CH{=}CH_2$	−32.0; −28.5;[a]	−30.1,	43.3; 43.5[a]	41.6,
			−29.1; −25.3[b]	−28.0	45.5; 46.1[b]	43.3
HCCH	OH_2	$HOCH{=}CH_2$	−29.0; −25.3;[c]	−24.5,	53.1; 52.2;[c]	50.9,
			−25.1;[h] −24.6;	−23.8	55.7;[h]	55.1
			−20.5[f]		58.3; 57.8[f]	
HCCH	FH	$H_2C{=}CHF$	−25.9; −22.7;[a]	−23.8,	50.2; 47.8;[a]	47.0,
			−19.2; −15.5[e]	−19.8	59.1; 57.2[e]	54.3
FCCF	OH_2	$CHF{=}CFOH$	−61.0; −57.8;[d]	−59.8,	33.8; 34.1;[d]	32.8,
			−59.4; −55.9[b]	−50.8	39.9; 41.1[b]	43.9
HCC	OH_2	$CH_2{=}COH$	−51.9[a]	−54.7,	22.8[a]	20.0,
				−48.5		20.7
HCCH	2 OH_2	$HOCH{=}CH_2$ +	−24.9;[c]	−25.9,	39.0;[c] 40.0[h]	36.7,
		H_2O	−27.5[h]	−17.4		31.2
FCCF	2 OH_2	$CHF{=}CFOH$ +	−56.4[d]	−62.9,	25.7[d]	23.3,
		H_2O		−62.0		27.0
HCC	2 OH_2	$CH_2{=}COH + H_2O$	−49.6[a]	−47.0,	3.7[a]	4.5,
				−46.4		−0.1

[a] B3LYP/B_1. [b] MP2/B_1. [c] B3LYP/B_4. [d] B3LYP/B_2. [e] MP2/B_3. [f] Stabilization of product as compared to H-bonded complex; left and right entries correspond respectively to ZPE-uncorrected and corrected values. [g] Energy barrier to pass from H-bonded complex to product. [h] B3LYP/B_2 single-point polarizable continuum model (PCM) calculations within the polarizable conductor calculation model (CPCM) for water solvent and assuming Pauling atomic radii. Reoptimization of the geometries within the CPCM framework affect energetics by less than 2 kcal·mol^{-1}. [i] First and second entries correspond respectively to B3LYP and G3MP2 values.

culated to adequately characterize stationary points and to evaluate the zero-point vibrational energies (ZPE). The latter was used to correct the binding energies, along with the counterpoise procedure.[19b,c]

Results

Binary Complexes. The first set of systems to be analyzed consists of each a series of molecules containing a triple C≡C bond, allowed to interact with a single additional molecule. The first event that occurs when those two molecules approach one another from infinity is the formation of a complex, in most cases connecting the two entities by a H-bond. This process was examined for our set of systems, via full geometry optimizations. The first three rows of Table 1 combine HCCH with each of NH_3, OH_2, and HF.[20−23] In each case, a linear CH···X H-bond is formed, as is illustrated in Figures 1−3, respectively. The properties of these H-bonds are reported in the first three rows of Table 1, inspection of which provides some interesting comparisons and excellent agreement with early results.[20] With regard first to the CH···X H-bond energies, this quantity is fairly small, less than 4 kcal·mol^{-1}. It is largest when X is N, the strongest proton acceptor, and smallest when X = F. The intermolecular H···X distances show much less variability from one X atom to the next, remaining in the range between 2.19 and 2.31 Å. The effect of the interaction upon the C−H covalent bond varies from a substantial stretch of up to 0.01 Å when X = N, to a very small contraction when X = F. The last column of Table 1 reveals that the C−H bond stretching frequency shifts to the red for all cases, with the magnitude varying as N > O > F, similar to the H-bond energy trends. Comparison of the last two columns reveals the very unusual situation for the HCCH···FH complex wherein the CH frequency shifts to the red but the C−H bond contracts. Removal of one of the H atoms from HCCH has little effect upon the CH···O H-bond, although it does significantly reduce the magnitude of the stretch of the covalent C−H bond. FCCF can obviously not donate a proton to water, so the resulting complex has water acting as donor to the electron-rich C≡C triple bond. This interaction is rather weak, with a binding energy on the order of only 1 kcal·mol^{-1}. Its weakness is reflected also in a very small stretch (by 0.001 Å) of the O−H covalent bond, and a red shift of its frequency of only 20 cm^{-1}.

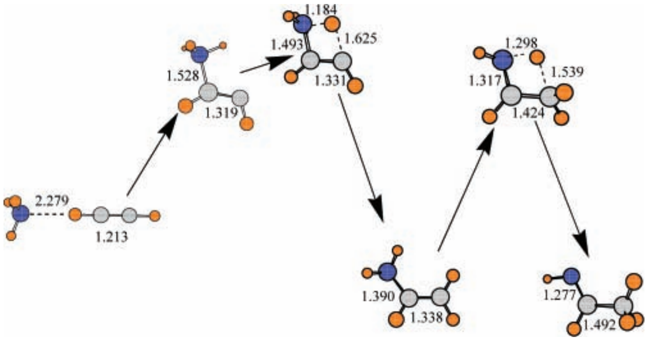

Figure 1. MP2/B1 potential energy surface (PES) of the bonding rearrangements within $HC\equiv CH\cdots NH_3$. B3LYP/B1 data are similar. Selected bond lengths are displayed in Å.

After the H-bond has been formed, there are succeeding steps that might be followed by each complex. For example, after forming a classical H-bond with one of the acetylenic H atoms, the NH_3 molecule moves off of the molecular axis and around toward one of the C atoms, in a sort of "rocking" motion. At the same time, the HCCH molecule distorts from its normal linearity, forming the NH_3CHCH entity illustrated in Figure 1.

Another important distortion of this species involves the C−C bond which elongates by 0.1 Å, relative to the H-bonded complex, as it loses its triple bond character. The latter complex lies some 38−40 kcal·mol^{-1} higher in energy than the original $HC\equiv CH\cdots NH_3$ H-bonded complex. The transition state separating these two (see Figure S1)[24] is very similar in character to NH_3CHCH, and only 2−4 kcal·mol^{-1} higher in energy. The completion of the anchoring of the NH_3 to the HCCH molecule occurs in the next step, wherein one of the H atoms from the NH_3 group begins to migrate toward the other C atom. This displacement encounters a barrier of some 6−7 kcal·mol^{-1}, before going down in energy by 70−76 kcal·mol^{-1}, to finally arrive at the $NH_2CH{=}CH_2$ alkene which is itself more stable than the original $H_3N\cdots HCCH$ complex by 25−29 kcal·mol^{-1}. The transition state for this H abstraction occurs near to the NH_3CHCH geometry and is characterized by a transition frequency ν_{tr}(N−H) of 1451 cm^{-1}, as the migrating H lies much closer (1.184 Å) to N, as compared to the 1.625 Å from the destination C. The C−C bond length in the final alkene molecule is 0.02 Å longer than in the NH_3CHCH entity, and the C−N bond is 0.14 Å shorter.

The energetics of this process are summarized in Table 2 wherein ΔE refers to the change in energy resulting from passing from the original H-bonded complex $H_3N\cdots HC\equiv CH$ to the single molecule $NH_2CH{=}CH_2$. The energy barrier for this process is listed in the penultimate column of Table 2 as $E^{\dagger}$. In this particular case, it is possible for another H atom to migrate from the N atom to the other C atom. This subsequent process, which converts the C═C double bond to single, is only slightly exothermic, ∼2−4 kcal·mol^{-1}, but encompasses a high-energy barrier of nearly 63−70 kcal·mol^{-1}.

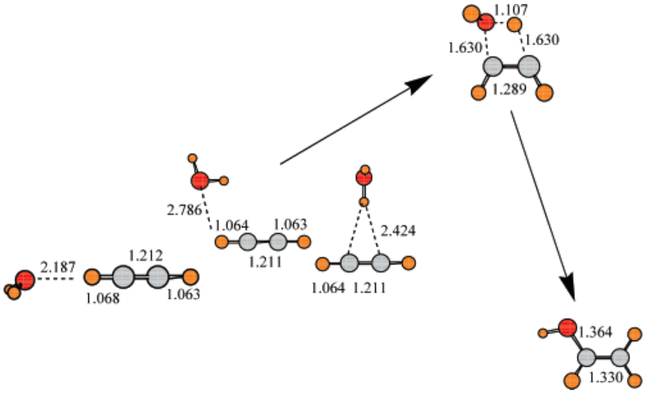

Figure 2. MP2/B4 PES of the bonding rearrangements within $HC\equiv CH\cdots OH_2$. B3LYP/B4 data are similar.

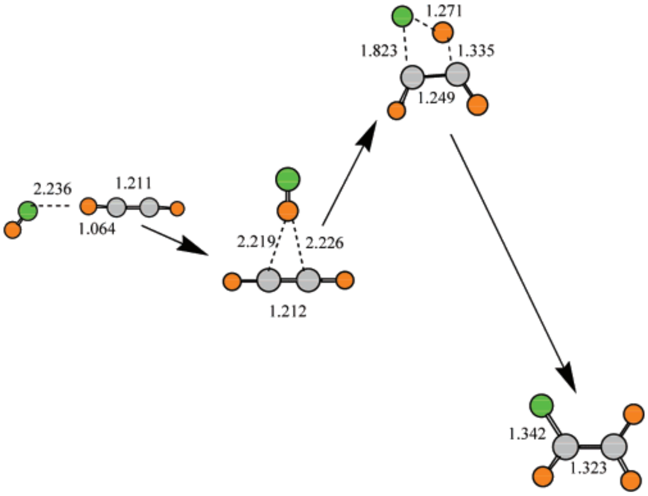

Figure 3. MP2/B3 PES of the bonding rearrangements within $HC\equiv CH\cdots FH$. B3LYP/B1 data are similar.

Replacement of NH_3 by a water molecule leads to a similar process but with some intriguing differences. As illustrated in Figure 2, after anchoring on to the terminal H atom of HCCH by a H-bond (a structure which corresponds to the Y(C_s) water-acceptor minimum of ref 22k and configuration (c) in Figure 1 of ref 22c), the water may migrate around so as to donate a proton to the electron-rich π-cloud of HCCH, transforming the original CH··O H-bond into a OH···π interaction (corresponding to the water-donor minimum T(C_s) of ref 22k). The two H-bonded configurations are very close in energy, and there is a very small barrier of less than 0.5 kcal·mol^{-1} (in perfect agreement with Table 6 of ref 22k) separating them that corresponds to the transition-state structure YT(C_1) of ref 22k. So for all intents and purposes, the three structures on the left side of Figure 2 may be considered as one freely interchanging H-bonded "manifold" that comprises a superposition of distinguishably different H-bonded states. To transform to the H_2CCHOH complex, the system passes through a transition state, in which the hydrogen has moved appreciably away from the water O atom, and toward the receptor C. This entire process is exothermic by 20−25 kcal·mol^{-1}, similar to that of the analogous NH_3 process. The barrier for the transformation from H-bonded complex to fully formed $HOCH{=}CH_2$ is a little higher for the water molecule, 52−58 kcal·mol^{-1}. It should be noted that immersion of the entire system in a dielectric continuum model of hydration ($\epsilon = 78$) has a very minor effect upon the aforementioned energetics, as detailed in Table 2. The replacement of H_2O by HF (Figure 3) yields a rearrangement to $H_2C{=}CHF$ that is somewhat less exothermic, but with a still high barrier of 48−57 kcal·mol^{-1}. As in the case of H_2O, the HF molecule also tends toward the $C\equiv C$ π cloud before its hydrogen separates from the F and moves toward the C atom.

Considering the rearrangement transition state, in which the hydrogen is in transit from X to the C atom, the X−H distance varies from 1.184 to 1.107 to 1.271 for X = N, O, and F, respectively. If one considers the ratio between this X−H distance, and the sum of (X−H + H−C) as a measure of the fraction of the total transfer within the transition state, these ratios are equal to 0.42, 0.40, and 0.49, for X = N, O, and F,

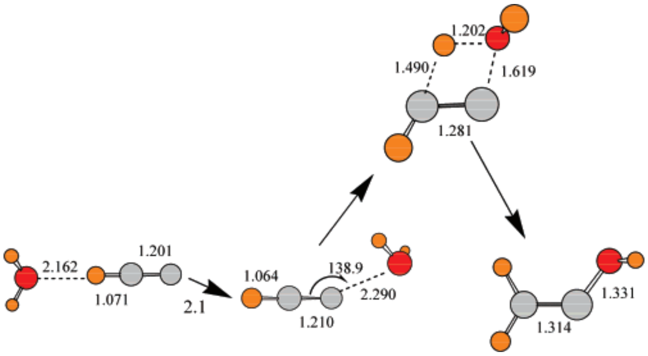

Figure 4. B3LYP/B1 PES of the bonding rearrangements within C≡CH···OH$_2$.

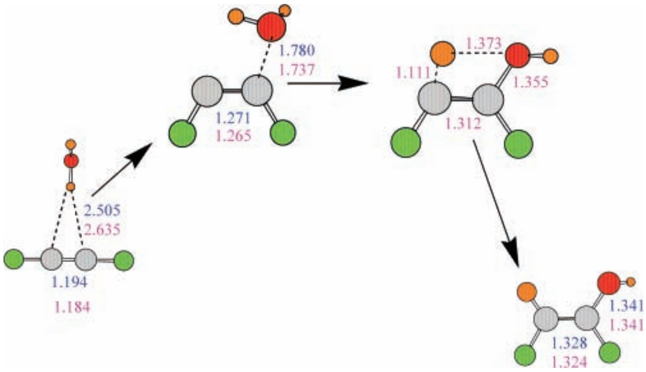

Figure 5. PES of the bonding rearrangements within FC≡CF···H$_2$O calculated at the MP2/B1 (selected bond lengths, in Å, shown in blue) and B3LYP/B2 (pink) levels.

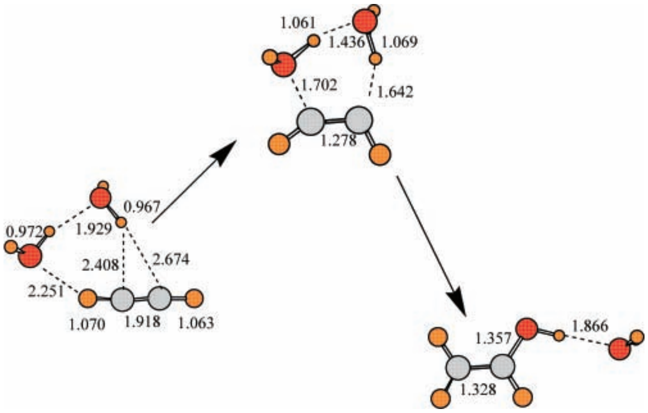

Figure 6. B3LYP/B4 PES of the bonding rearrangements of HC≡CH + 2H$_2$O.

respectively. All in all, there is not a great deal of sensitivity of these geometrical parameters to the nature of the X atom.

As indicated above, the absence of H atoms on FCCF precludes the water molecule from acting as proton acceptor in the initial complex. The most stable complex thus contains a OH···π interaction between the water and the π system of FCCF, as illustrated in Figure 5. The rearrangement involves first a rotation of the water molecule, placing the water O atom and one of the C atoms of FCCF within about 1.8 Å of one another, with no bridging H. One of the water H atoms then moves away from O and approaches the other FCCF C atom. This process encounters an energy barrier on the order of 34−41 kcal·mol^{-1}, lower than that of the HCCH···OH$_2$ system. The entire rearrangement process is exothermic by close to 60 kcal·mol^{-1}, nearly double that of the HCCH analogue.

Instead of replacing the H atoms of HC≡CH by F, one might consider also the result of removing one H atom, leaving behind a HC≡C radical, as pictured in Figure 4. The appropriate row of Table 2 reveals that this removal doubles the exothermicity of the rearrangement from 25 kcal·mol^{-1} to more than 50, drawing a parallel to FCCF. This alteration also drastically cuts the barrier down to 23 kcal·mol^{-1}, about half of what it was for HC≡CH. Whereas the initial H-bonded complex in Figure 4 is similar for HCCH and HCC, both complexes undergo a motion of the water molecule relative to the alkyne, involving little energy change, as a prelude to the proton transfer. The transition states for the rearrangement are also similar, at least geometrically. Some recent calculations[25] support the data computed here. Ding et al.[25] had computed a total rearrangement energy ΔE of −49.2 kcal·mol^{-1} at the CCSD(T)/6-311+G(2d,-2p) level (not including ZPE), not very different from our value of −51.9 kcal·mol^{-1}. The energy barriers for the rearrangement are a little different, 28.7 kcal·mol^{-1} [25] (without ZPE) as compared to our value of 22.8 kcal·mol^{-1}. In summary, then, the most exothermic rearrangements occur when either FCCF or HCC is paired with a water molecule; the lowest barrier to this rearrangement is associated with the latter.

From a methodological perspective, comparison of the data presented in Tables 1 and 2 leads to certain conclusions. In the first place, B3LYP H-bond energies tend to be somewhat smaller than those computed via MP2, given the same basis sets. The overall stabilization that accompanies the rearrangement of the H-bonded complex to form the final product is only very slightly overestimated by B3LYP as compared to MP2. The B3LYP energy barriers for this rearrangement step are consistently higher than MP2.

Ternary Complexes. As indicated above, there is the possibility of a somewhat different mechanism when another small molecule is added to the system. The last three rows of Table 1 refer to ternary systems in which a second water is added. The H-bond connecting the two waters is stronger than the interaction with the C≡C containing system, so distortions of H-bond geometry are to be expected. Indeed, the previously linear CH···O arrangement in HCCH···OH$_2$ is bent by 36° when the second water is added, as indicated in Figure 6. The value of 7.0 kcal·mol^{-1} reported in Table 1 for the H-bond energy of this system refers to the total interaction energy of the entire trimer, and so also includes both the OH···O bond connecting the two waters and a presumably weak OH···π bond between the HCCH and second water. Comparison with the data concerning HCCH plus a single water molecule, shows that the presence of the second water lengthens the CH···O bond. It also greatly reduces the stretch induced in the C−H covalent bond, and the red shift of its stretching frequency is diminished by a factor of 3. The newly introduced OH···π bond stretches the O−H covalent bond of the relevant water and shifts its stretching frequency to the red by 38 cm^{-1}. When a second water is added to the FCCF···OH$_2$ system, it has little effect upon the geometry of the complex, simply acting as a proton donor to the first water, as indicated in Figure 7. Adding a second water to CCH···OH$_2$ again causes an angular distortion, as illustrated in Figure 8. The CCH unit is apparently more flexible than its HCCH cousin, in that a 15° deviation from linearity occurs within this entity. The relevant C−H bond is also significantly stretched, by 6 mÅ, and its stretching frequency diminished by 125 cm^{-1}, an even larger red shift than occurs in the O−H bond of the water.

The last three rows of Table 2 refer to the rearrangement process that follows the formation of the initial ternary complex. It may first be noted that this second water molecule scarcely affects the overall ΔE for the rearrangement process, which is

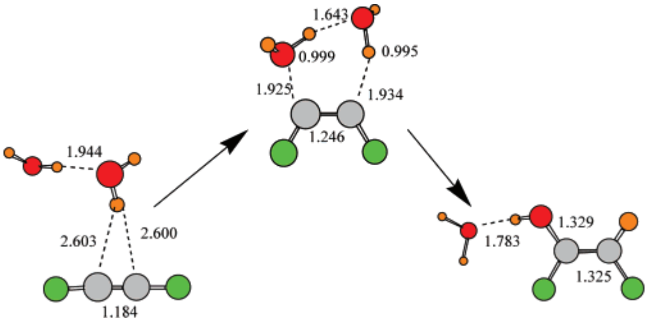

Figure 7. B3LYP/B2 PES of the bonding rearrangements of $FC\equiv CF + 2H_2O$.

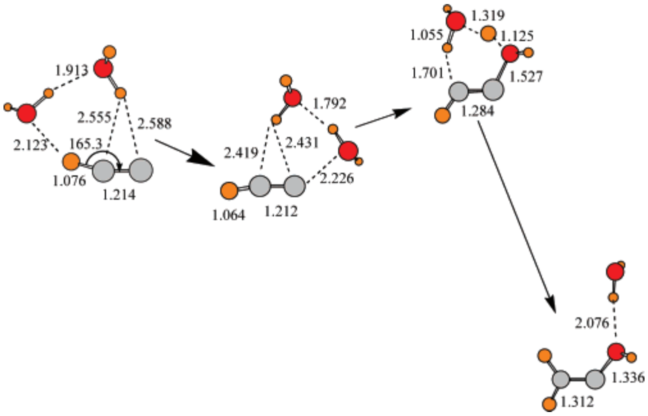

Figure 8. B3LYP/B1 PES of the bonding rearrangements of $C\equiv CH + 2H_2O$.

not surprising. More important, however, is the effect upon the barrier. The presence of this second water drastically reduces the barrier. For example, the rearrangement barrier for HCCH, when coupled with a single water molecule, was found to be 52−58 kcal·mol^{-1}, but this quantity is lowered to 39 kcal·mol^{-1} by the second water. (The transition from a gas phase to an aqueous environment has only very minor effects upon the energetics of the process.) Likewise, the barrier for FCCF drops from 34 to 41 kcal·mol^{-1} down to 26. Most remarkable of all is the result for the HCC radical where the barrier is reduced below 4 kcal·mol^{-1}. Again, the transition from a gas phase to an aqueous environment has only very minor effects upon the energetics of the process.

Examination of the pathways for these rearrangements provides some insights into the underlying reason for these barrier reductions. In all cases, the transition state for the rearrangement process corresponds to a proton transfer from a water O atom to the C atom of the original alkyne. When only one water molecule is present, this transition state is a high-energy entity, as the proton is moving along a highly deformed H-bond. In the HCCH case, for example, the θ(O···H···C) angle is 112°, quite distorted from a preferred linear arrangement. The second water acts as a shuttle, accepting one proton while releasing another. This combination permits the two relevant H-bonds to remain fairly close to linearity. Again taking HCCH as our example, the θ(OH···O) and θ(OH···C) angles are respectively 161° and 150° in the transition state, a far more favorable arrangement. The two-water structure also permits the two covalent bonds that must be ruptured by the proton motion to stretch by a smaller amount in the transition state. The O−H distance in the single-water case is 1.107 Å, as compared to O−H distances of only 1.061 and 1.069 in the two-water transition state. Very similar principles are in operation in the FCCF and CCH cases. The θ(O···H···C) angle is 101° in the single-water transition state for FCCF, 118° for CCH.

Conclusions

H-bonds are commonly viewed as stable in a global energetic sense: the ground electronic state of a given conventional H-bonded system is taken as the energy minimum on the full PES and is thus experimentally detectable. Of course, it is understood that there might be some exceptional cases, but the foregoing is the normal situation. Unconventional H-bonds of the C≡C−H···X type are substantively distinct. Although the lifetimes of these complexes might be sufficiently long that they may be detected experimentally, they are thermodynamically unstable in the sense that they are not global minima on the potential energy surface.[26,27] After forming the H-bonded complex, an atomic rearrangement that splits apart and incorporates the partner subunit into a single molecule can reduce the triple C≡C to a double bond, yielding an even more stable system. Indeed, this lowered energy is substantial, typically on the order of 20−50 kcal·mol^{-1}. On the other hand, the rearrangement process is impeded by a sizable energy barrier, ranging between 30 and 60 kcal·mol^{-1}, so this reaction is not normally observed. If, however, a second solvent molecule is added to the complex, the situation can change dramatically. This second molecule can catalyze the process by serving as a bridge that relays a proton from one part of the rearranging complex to another.[28] In doing so, the energy barrier is strongly reduced, and the rearrangement becomes kinetically viable. In the most extreme case considered here, involving the HCC radical, the second water molecule reduces the rearrangement barrier from more than 20 to less than 4 kcal·mol^{-1}. It might finally be noted[29] that the rearrangement of H-bonded complexes to entirely different species is not an entirely unknown phenomenon, when containing a radical species. This work has addressed uncharged species; it is conceivable that cationic or anionic systems may have even smaller rearrangement barriers.

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Supporting Information Available: More complete descriptions of all stationary states. Figures 1−8 of the present work correspond to a more complete low-energy portion of the corresponding PES displayed in Figure S1−S8 (see also ref 24). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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