Competition between Lone Pair-π, Halogen Bond, and Hydrogen Bond in Adducts of Water with Perhalogenated Alkenes $C_2Cl_nF_{4-n}$ (n = 0-4)

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ABSTRACT

A thorough search of the potential energy surface is carried out for heterodimers of water with $C_2Cl_nF_{4-n}$. Three different types of interactions are observed. Structures dominated by a lone pair-π interaction have the highest binding energies, and are stabilized by charge transfer from O lone pairs of H_2O to the C-C π* antibonding orbital of the alkene. Halogen-bonded O··Cl complexes are slightly less strongly bound, followed by OH··X hydrogen bonds. The replacements of Cl by F atoms have only small effects upon binding energies. Inclusion of vibrational and entropic effects removes the clear energetic superiority of lp-π binding energies. When combined with the observation of several similar geometries for each particular heterodimer type, and a sensitivity to basis set, it would be quite difficult to predict with any degree of certainty the single most stable configuration, even with very high level calculations.

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INTRODUCTION

A variety of noncovalent interactions have been recognized over the years[1-4]. Of those, hydrogen bonds (HBs) are usually considered the most widespread and important, leading to their thorough study [5,6]. The original consideration of N, O and F as HB donor and acceptor atoms has been expanded to include other less electronegative atoms like P, S, Cl and even C. [7-14]. Replacement of the bridging H by a halogen atom leads to another type of strong noncovalent bond. Like the HB, this halogen bond [15-22] is stabilized by charge transfer into a σ^* orbital, coupled with electrostatic attraction. Pnicogen and chalcogen atoms (e.g. P and S) can replace the halogen, engaging in their own eponymous bonds [23-36].

In addition to lone pairs, another source of electron density for HBs can be associated with π bonds. NH···π, CH···π, and OH···π HBs are prominent examples, covering a wide range of strength, and occurring in a diverse array of systems [37-43]. The most common π systems that engage in such interactions are delocalized aromatic groups and C=O bonds [44]. Charge transfer from a π system is not limited to HBs, but is more general. For example, a recent study [45] showed that π-systems of some simple alkenes can donate charge to a P-X σ^* antibonding orbital, forming a P···π interaction.

Just as the occupied π bonding orbitals can serve as an electron source, so can vacant π^* antibonding orbitals act as a sink. Lp-π interactions in which the complex is stabilized by charge transfer from lone pairs to a π^* orbital have been observed in a number of different settings. Whereas an OH···π HB is the most stable interaction for benzene-water, it is a lp-π bond which becomes the dominant force in the hexafluorobenzene-water heterodimer [46]. Such lp-π interactions are seen not only in small molecular systems but also [47] in the crystal structures of nucleic acids and proteins. A combined cation-π and lp-π interaction was observed [48] in some crystal structures containing H_3O^+ units. Nitrogen lone pair···π interactions were observed between amine and tri-s-triazine derivatives and were found [49] to be as strong as 9.8 kcal/mol. Besides O and N lone pairs, those of S, P, F and Cl also participate [50] in lp-π interactions. π^* electron acceptors are not limited to lone pair donors. For example, the stacking of two amide units is stabilized by transfer from the π(CO) orbitals of one amide to π^*(CO) of its partner [51], making this sort of bonding pattern nearly as strong as a NH··O HB formed between the same units.

Many of the relevant prior observations of lp-π bonds involve a polar C=O bond which accepts charge into its π^* orbital, and usually asymmetrically in that the donor is poised over the C atom. The charge may originate in the lone pairs of O [52-55], N, [56-58] or even S [59]. In addition to any charge transfer effect, many of these interactions undoubtedly owe a great deal of their stability to the Coulombic attraction between the approaching negatively charged donor (O, N, or S) and the positive charge associated with the C end of the carbonyl. Indeed, there is some sentiment that these interactions might better be characterized as dipole-dipole, as opposed to charge-transfer [60,61].

This sort of electrostatic effect would be attenuated in a more symmetric C=C π system as electron acceptor, as in an alkene, such that any attraction can be attributed directly and less ambiguously to a lp-π charge transfer. However, an unsubstituted alkene such as ethylene has a negative electrostatic potential above its plane that would repel any approaching lone pair donor. Replacing the H atoms by electron-withdrawing agents such as halogen atoms would pull electron density out of the π area, and permit the approach of a lone pair donor. As a secondary benefit, a halogenated alkene offers several competing options which can then be compared with a lp-π bond. In the first place, the lone pairs of the partner molecule can engage in a halogen bond with each of the halogen atoms. These same halogens also offer an electronegative site, with its own lone pairs, which can act as proton acceptor in a HB with the partner molecule.

For these reasons, the present work concerns a series of halogenated alkenes. Beginning with $Cl_2C=CCl_2$, one Cl atom after another is replaced by F, in order to systematically compare the two halogen atoms. While F is more strongly electron-withdrawing, it does not readily engage in halogen bonding. But at the same time, F would serve as a superior HB proton acceptor. Water was chosen as a partner molecule for a number of reasons. Although the lone pairs of any electronegative atom might participate in a lp-π interaction, H_2O is widely considered as a model for various noncovalent interactions due to its importance in various chemical and biological systems [62,63]. H_2O is a universal solvent and is present as a major ingredient in biological systems. H_2O can act as both electron and proton donor. It is known to engage in the three sorts of interactions of interest here: lp-π with various π-systems, O···X halogen bonds, and of course OH··X HBs [43,64].

There have been no previous experimental determinations of the structures of complexes pairing water with a perhalogenated alkene. The sole exception is a very recent report [65] that dealt with one particular case of C_2Cl_3F. The authors identified six possible dimer geometries via their calculations, one of which appeared to represent the structure observed in the rotational spectrum, or at least to be consistent with that spectrum. However, in addition to uncertainty as to the details of the geometry, there was little analysis of the nature of the bonding in this complex, nor of any of the secondary minima. Moreover, as described below, the results obtained with the basis set employed are of questionable accuracy. Nonetheless, we are encouraged that the authors found experimental evidence that a lone pair-π complex with the water molecule is likely the preferred conformation in the gas phase, adding confidence to our own findings that are reported below.

COMPUTATIONAL METHODS

Calculations were performed using the Gaussian-09 package at the MP2/aug-cc-pVTZ level of theory [66]. The potential energy surface of each $H_2O/C_2Cl_nF_{4-n}$ heterodimer was searched to find all possible minima, which were verified by the presence of all positive frequencies. Binding energies were calculated as the difference in energy between the complex and the sum of the pair of isolated optimized monomers, and were corrected for basis set superposition error by the counterpoise procedure [67]. Natural Bond Orbital (NBO) analysis [68,69] was performed by using the procedure contained in Gaussian. Symmetry Adapted Perturbation Theory (SAPT) was carried out via the Molpro suite of programs [70].

RESULTS

The first exposure of a molecule approaching one of these halogenated alkenes arises from the electrostatic field surrounding it [71-74]. These potentials are exhibited in Fig 1, on a surface corresponding to twice the van der Waals radius of the various atoms. The most positive regions are indicated by blue and the red areas correspond to negative potential. In general, there are blue positive regions directly above each C=C bond, as well as near to Cl atoms, along extensions of the C-Cl bonds. Both of these sections can attract the partially negatively charge O atom of HOH. Negative potentials will tend to attract the H atoms of HOH. These red areas lie in the molecular plane, particularly close to F atoms. Closer inspection reveals that the most negative areas lie not directly along any C-X bond, but rather off to the side, consonant with the idea of several lone pairs on each halogen atom.

Given this pattern of electrostatic potential, one might anticipate three different sorts of geometrical dispositions. The O atom may approach the Cl atoms directly along the C-Cl bonds in a classic halogen bond arrangement. Alternately, the water may be drawn above the molecular plane, with its O atom pointing down toward the C=C bond region. A third primary geometry would consist of H-bonds, of the OH··F and OH··Cl sorts. And indeed, all of the minima identified in the potential energy searches fall into one of these three categories. More specifically, the potential energy surface of each of the $C_2Cl_nF_{4-n}\cdots H_2O$ (n = 0 - 4) systems was searched thoroughly to find the structures of all possible minima. Four different complexes were obtained for C_2Cl_4, 9 for C_2Cl_3F, 14 for $C_2Cl_2F_2$, 6 for C_2ClF_3, and only one for C_2F_4, for a total of 34 in all.

Out-of-Plane Configurations:

The most stable sort of complex is that in which the HOH molecule lies above the alkene plane. These geometries are displayed in Figs 2 and 3 where it may be noted that there is in general more than one minimum for each alkene. The energies of these minima are not very different from one another, as may be seen by the counterpoise-corrected binding energy displayed for each in the figures. Considering the most stable of each set, the binding energies all lie in the fairly narrow range between 2.1 and 2.4 kcal/mol. The gem-$C_2F_2Cl_2$ forms the tightest complex with water, and CF_4 the weakest.

The water molecule is generally oriented so that its negatively charged O atom approaches toward the C=C bond, either near its center or shifted off toward one C atom or the other. One of the water H atoms tends toward the halogens of the alkene, taking advantage of any negative potential in this region. Scrutiny of Fig 1 shows an intensifying blue color as more Cl atoms are replaced by F. This trend is a result of the strongly electron-withdrawing power of F that draws density out of the region above the molecular plane, making it progressively more positive. This trend is also apparent in the three $C_2Cl_2F_2$ molecules, where the gem variant has the most positive region directly above the CF_2 group. There is a loose correlation between the intensity of the blue region in Fig 1 and the interaction energy in the first row of Table 1. For example the complex with gem-$C_2Cl_2F_2$ is more strongly bound than the cis or trans conformers. On the other hand, even though the potential is most positive directly above the C_2F_4 molecule, its binding energy with water is the smallest of all dimers. Clearly then, the Coulombic interaction between the negative water O and the positive region above the alkene plane is only one component of the interaction.

Most of these structures are also stabilized by a charge transfer from the O lone pairs into the π* antibonding orbital of the alkene. The NBO estimate of this transfer energy E(2) is reported in Table 1 where it may be seen to be largest for gem-$C_2F_2Cl_2$ consistent with its strongest binding energy. (The contributions of both O lone pairs are combined therein.) On the other hand, the smallest value of E(2) in Table 1 occurs for C_2Cl_4, even though it is C_2F_4 which is most weakly bound. (Values for all minima, not just the most stable of each pair, are listed in Table S1 of the Supplementary Information section.) Clearly then, like the Coulombic energy, E(2) is also not the sole quantitative arbiter of the binding energy.

One reason for the lack of strict correspondence between the binding energy and the two factors above is the possibility of a second stabilizing interaction, beside the $O_{lp}\rightarrow\pi^*(CC)$ charge transfer. In most complexes, one can observe a tilt of the water molecule such that one of its protons points in the general direction of a halogen atom. This tilt is largely the result of a Coulombic attraction between the water proton and a negative region of the electrostatic potential near the halogen of the alkene. Complex 1c is a bit of an extreme, in that it shows evidence of a weak HOH···Cl H-bond. The R(H··Cl) distance of 2.788 Å is complemented by a NBO E(2) of 0.26 kcal/mol for $Cl_{lp}\rightarrow\sigma^*(HO)$.

It may be noted from Figs 2 and 3 that in some cases the water O takes up a position directly above the C=C midpoint, while in others it is poised above one or the other C atom. This position results in a fine balance between several phenomena. For example, it is clear from Fig 1 that the two electron-withdrawing F atoms of the gem-$C_2F_2Cl_2$ induce a greater positive charge above CF_2 than above the CCl_2 portion, which pulls the water in that direction; likewise for $CClF_3$. A second factor which opposes a central position of the water is the attraction of the water protons toward the electronegative halogens, as is plain in 1p. More specifically, when the water H atom is drawn toward a Cl atom, the O remains approximately centrally poised between the two C atoms, maximizing its lone pair → π* charge transfer. In contrast, the O atom moves away from this central location when the water H is drawn toward a F atom. Apparently, the more negative electrostatic potential around F, as compared to Cl, is strong enough to counter the competing tendency of the $O_{lp}\rightarrow\pi^*$ transfer toward a central position.

In summary, there are a number of factors that influence the energetics of the various structures. The O and H atoms of water are attracted respectively toward positive and negative regions of the alkene's electrostatic potential. A strongly asymmetric electrostatic potential, as that above gem-CCl_2CF_2 can pull the water away from the center and toward the more positive CF_2 group. Charge transfer from the O lone pairs into the π* antibonding orbital of the alkene is pivotal, but can be supplemented, or even replaced, by transfer from the halogen lone pairs into the OH σ* orbital, in the form of a OH··X H-bond. This sort of interaction will also pull the water away from a central position above the alkene.

The last two rows of Table 1 report the values of the thermodynamic quantities ΔH and ΔG for the association reaction. The former is somewhat less negative than is ΔE due primarily to the influence of zero-point vibrational energies. ΔH varies between -1.44 and -1.92 kcal/mol, with the most negative associated with C_2Cl_3F. Note that the inclusion of the vibrational effects alters the energetic ordering of ΔE which was most negative for gem-$C_2F_2Cl_2$. The further addition of entropic effects leads to the ΔG quantities in the last row of Table 1. ΔG follows a different pattern than either ΔE or ΔH. For example, while gem-$C_2F_2Cl_2$ has the most negative value of ΔH, it has the most positive ΔG. Detailed comparison of the various minima for each substituted alkene also displays some energetic reversals. Table S1 reveals, for example, that whereas structure 1a containing a $O_{lp}\rightarrow$C-C π* transfer, is preferred over the OH··Cl H-bond of 1b in terms of ΔE and ΔH, it is 1b that has the lower ΔG. It seems apparent that a simple evaluation of the binding energy ΔE, even if highly accurate, may not be the final arbiter of the relative stability of the various dimers.

Complexes Containing a Halogen Bond

In addition to the positive potential located above the C=C bond, there is another positive region near each Cl atom, along the extension of the C-Cl bond. The O atom of water is drawn to this position to form what is commonly referred to as a Cl··O halogen bond. Minima with this arrangement are illustrated in Fig 4 where it may be seen that there is one such structure for each unique Cl atom. In keeping with the usual expectations for halogen bonds, the θ(C-Cl···O) angle is close to 180° in all cases. There is only a small variation in complexation energies, varying from a minimum of 1.69 kcal/mol for gem-$C_2F_2Cl_2$ up to 1.92 kcal/mol for C_2Cl_3F. Likewise, the R(Cl··O) distances are also rather uniform, in the 2.975 - 2.986 Å range, with shorter distances corresponding to stronger binding. The absence of any F··O halogen-bonded minima is notable, and not surprising given the rarity of such interactions, amplified by the absence of positive electrostatic potential regions along the extensions of C-F bonds (see Fig 1).

Some of the energetic and geometric parameters of the O···Cl halogen bonded minima are reported in Table 2 (all are reported in Table S2). The NBO E(2) values corresponding to charge transfer form O lone pairs to the C-Cl σ* antibonding orbital are all equal to approximately 1.1 kcal/mol for each of these complexes, and the charge transfer Δq falls in the range of 1.3 - 1.5 me. The values of ΔH follow the same pattern as ΔE, although slightly less negative. ΔG, on the other hand, obeys a different trend. Even though gem-$C_2Cl_2F_2$ has the least negative value of ΔE or ΔH, ΔG for its association with HOH is least positive, and vice versa for C_2Cl_3F. Comparison of the energetics in Tables 1 and 2 show that the O-π interactions are stronger than halogen bonds in the context of ΔE and ΔH, but that the halogen bonds are favored with respect to ΔG.

Complexes Containing Hydrogen Bonds

The electrostatic potentials in Fig 1 show negative as well as positive regions, which would tend to attract a H atom of the water. These red areas are more intense around F than Cl, and are most negative when off to the side of the C-X axis. This shape helps explain the configuration of the minima displayed in Fig 5 wherein the H atom generally takes a position close to two different halogen atoms, in what might be denoted as a bifurcated H-bond. These systems can be nearly symmetric as in 3a, but are more commonly asymmetric as in 3b, 3e, etc. R(H··F) distances are characteristically shorter than R(H··Cl) which is consistent with the more negative electrostatic potentials around the F atom.

The binding energies in Table 3 are somewhat weaker than the halogen bonds in Table 2, with $-\Delta E$ between 1.3 and 1.7 kcal/mol. The values of E(2) for the $X_{lp}\rightarrow\sigma^*(OH)$ charge transfer are consistent with the presence of a weak H-bond, as are the NBO charge shifts Δq. The most strongly bound complexes in Table 3 are associated with the C_2Cl_3F and cis-$C_2Cl_2F_2$ alkenes. Note that the perfluorinated C_2F_4 does not form a H-bonded complex with water, which is consonant with the lack of a clear negative potential in Fig 1g. The strength of each complex can be considered to be a resultant of both electrostatic and charge transfer considerations. While the ΔH pattern of Table conforms to ΔE, ΔG again displays contrary behavior. Although C_2Cl_3F and cis-$C_2Cl_2F_2$ have the most negative values of ΔE and ΔH, their values of ΔG are most positive, surpassed only by C_2ClF_3. (Data for all H-bonded minima are presented in Table S3.)

Interactions not Present

Given the large number of minima identified in these potential energy surfaces it is perhaps surprising that none correspond to a OH···π interaction, a phenomenon which is known to occur widely. The likely reason for this absence derives from the electrostatic potentials of Fig 1. The halogen substituents draw charge away from the π region above the alkene molecular plane, imbuing this region with a positive potential, which acts to repel the water proton. While there are several structures containing what may be described as OH··X H-bonding, these structures are all bifurcated to some degree. In other words, there are no OH··X interactions which are not simultaneously accompanied by a second such attraction, or a $O_{lp}\rightarrow\pi^*$(CC) interaction. Notable in its absence as well is the lack of any H-bonded minimum between HOH and C_2F_4. This absence if likely due to the very positive electrostatic potential above the alkene molecular plane (Fig 1g). It would appear that any water initially placed in a position to engage in any such OH··F H-bond would be more strongly attracted out of the alkene molecular plane where the negative water O can interact with the positive region of the alkene. And as indicated earlier, the same C_2F_4 molecule fails to engage in any halogen bonding minima.

Electron Density Shifts and Energy Decomposition

One may glean fundamental information about molecular interactions by monitoring the shifts of electron density that occur. Fig 6 displays these shifts for each sort of configuration as the difference in density between the complex, and the sum of the densities of the isolated monomers. Increases in density arising from the formation of the complex are shown in blue, and losses in red. The strongest interaction of the $O_{lp}\rightarrow\pi^*$ variety occurs for the gem-$C_2Cl_2F_2$ alkene and its density shifts in Fig 6a include first an increase around the lone pair region of O of H_2O. Also evident is a loss in the alkene π region near to the water, and an accompanying increase in the π region on the opposite side of the alkene. Other changes include a loss around the two water protons, and an increase on all of the alkene halogens. The overall left-to-right shift in Fig 6a is consistent with the transfer of charge from water to the alkene.

The pattern in Fig 6b, involving C_2Cl_3F, is consistent with other halogen bonds in the literature [75,76]. The pattern around the halogen-accepting water molecule is quite similar to that in Fig 6a. There is a region of loss to the left of the halogen and some gain to its right, in the Cl-C bonding area.

Also beneficiaries of additional density are the peripheral X atoms. The overall direction of shift in Fig 6b is from left to right, as in Fig 6a. The H-bonded structure of this same alkene is illustrated in Fig 6c. Its H-bonded character is verified first by the density loss around the bridging proton of water. Further confirmation comes from the density gains to the left of the two proton-accepting halogen atoms. Unlike the lp-π and halogen bonds, the charge shifts from right to left in H-bonded conformation 3b.

Another window into the nature of each interaction can be opened via decomposition of the total binding energy into various components. SAPT decomposition of the most stable minimum of each of the lp-π interaction, halogen bond and hydrogen bond dimers are presented in Table 4, where ES refers to the Coulombic interaction between the charge clouds of the two subunits and EX to their Pauli exchange repulsion. Induction (IND) represents the stabilization occurring from perturbations in the electron distribution of each monomer induced by its partner, comprising both polarization and charge transfer. The instantaneous charge fluctuations and their effects upon the partner are contained within the London or dispersion (DISP) term. Exchange-induction (EXIND) and exchange dispersion (EXDISP) represent higher-order contributions. For the lp-π interaction and halogen bonding, ES is the major contributor accounting for nearly 45% of attractive contributions followed by DISP (31%) and IND (24%). The H-bonded complex is different: DISP displaces ES as the major attractive contributor with 42%, followed closely by ES (37%) and IND (21%). ES and EX are nearly equal in magnitude in the former two interactions, whereas EX is larger than ES in the H-bonded complex.

Effects on Internal Structures

Given the charge transfer into the C=C π* antibonding orbital, one would anticipate that the C=C bond would elongate upon formation of the lp-π complexes. Surprisingly, however, the first row of Table 5 shows that this bond contracts in all cases, by some 1-2 mÅ. This indication of bond strengthening is verified by the increases in the stretching frequency by 5-9 cm^{-1}. The next four rows provide a means of understanding this apparent paradox. The occupancy of the C=C π* antibonding orbital diminishes which would act to shorten the C=C bond. The same is true of the bonding orbital occupancy, but by a smaller amount, so the net result of these two effects is the observed bond contraction. The next two rows of Table 5 indicate very minimal changes in the σ and σ* C=C orbitals, all less than 1 me, so the σ system will have little effect upon the C=C bond length. If there is charge transfer into the π* orbital, but its occupancy goes down, where does it actually go? The next row of Table 5 shows that the charge being transferred into the alkene makes its way to the lone pairs of the various halogen atoms, whose total population increases by 3-6 me. The last row of Table 5 presents the stretches of the O-H bond, which suggest at least a weak HB, which supplements the lp-π bond.

Turning next to the halogen-bonded dimers, there is the usual expectation that the charge transfer into the σ*(C-X) antibond will lengthen this bond. Again, however, these complexes defy the usual rule. The first row of Table 6 indicates a shortening of the C-Cl bonds by 1-3 mÅ. The following row shows that the pertinent vibrational frequencies are relatively constant, changing by less than 1 cm^{-1}. The σ*(C-Cl) orbital occupancy changes are surprisingly small, all well below 1 me, and not of uniform sign. The changes in the bonding orbital are also small, albeit larger than those of the σ* orbital, but uniformly negative. This small net loss of bonding thus cannot account for the C-Cl bond contraction that is observed. Formation of the halogen-bonded complexes produce negligible changes in the C=C bond of the alkene, with bond length changes of less than 1 mÅ.

The next row of Table 6 shows that the charge transferred from the water into the σ*(C-Cl) orbital does not remain there, but continues on into the lone pairs of the peripheral halogen atoms. What would be the result were there no such halogen atoms to receive this charge? In order to answer this question, computations were carried out for the halogen-bonded complex of H_2O with $CClH{=}CH_2$. As reported in Table S4 in the Supplementary Information, this halogen bond is roughly half the strength, with ΔE= -1.0 kcal/mol, and with $O_{lp}\rightarrow\sigma^*$(Cl-C) E(2) of only 0.60 kcal/mol. As in the perhalogenated cases, the C-Cl bond contracts, by 3.1 mÅ, indicating no loss of the degree of C-Cl bond shortening by replacing the halogens by H. Also similar, the populations of the σ and σ* C-Cl orbitals are changed little as a result of complexation. Whereas the peripheral halogen atoms of the molecules in Table 6 were able to accumulate between 5 and 9 me of additional density, the H atoms of $CClH{=}CH_2$ can hold much less, a total of roughly 2 me, in their combined σ and σ* orbitals. Helping make up for this deficiency, the π*(C=C) antibonding orbital of $CClH{=}CH_2$ is the beneficiary of an additional 3.0 me, a change which is not observed in the perhalogenated analogues. In summary, the replacement of peripheral halogen atoms by H leaves the C-Cl bond contraction in place, as well as the near constancy of the σ*(C-Cl) orbital occupancy. Rather than accumulate on the peripheral halogen atoms, the charge transferred from the water winds up largely in the C=C π* orbital, where it elongates the C=C bond by 0.82 mÅ.

This finding begs the question as to what might happen in the absence of a C=C double bond. For this purpose, the same sort of calculations were carried out, replacing $CClH{=}CH_2$ by the $CClH_2$-CH_3 alkane. As reported in the last column of Table S4, the O··Cl halogen bond here is very weak indeed, with a near zero binding energy, and E(2) amounts to only 0.3 kcal/mol. As in the other cases, the C-Cl bond is shortened, in this case by 1.5 mÅ. In the absence of C=C π and π* orbitals as density sinks, this alkane displays a larger growth in the σ*(C-Cl) orbital population than does the alkene, which partially accounts for the bond shortening.

In most cases, the orbital population changes are inconsistent with the contractions of the C-Cl bond. In order to resolve this contradiction, a second factor was considered. The Bent rules [77-81] suggest that bond lengths are dependent not only upon charge transfer (hyperconjugation) but also rehybridization of the bonding orbitals. Examination of the sp^n hybridization of the NBO C-Cl bonding orbitals around the central C atom for the various alkenes examined here shows that n undergoes a small decrease upon complexation. This lowering corresponds to a 0.7% enhancement of s-participation which is associated by Bent's rule with a small contraction of the C-Cl bond. Changes of this same magnitude, and even smaller, have been associated with shortening of other bonds as well [82,83]. It would appear then that the changes in C-Cl orbital populations that occur when an alkene participates in a halogen bond are small enough that they are outweighed by rehybridization effects, thereby leading to a shortening of r(C-Cl).

Sensitivity of Results to Computational Method:

As noted above, there are only small energy differences separating some of the minima on each potential surface combining water with a given substituted alkene. Moreover, the most favorable minimum with respect to ΔE may be different in the context of ΔH or ΔG. Not surprisingly, then, the relative energies of the minima are also sensitive to the precise level of theory applied. The calculations presented above were performed using the MP2 method in conjunction with the aug-cc-pVTZ basis set, generally considered an accurate level for these sorts of interactions.

As an example of the sensitivity to basis set, a recent experimental and theoretical study [65] used the somewhat smaller 6-311++G** basis set with the MP2 method to find the possible minima pairing C_2ClF_3 with H_2O and identified six different structures. The results were limited to ΔE, with no evaluation of ΔH or ΔG. The most stable minimum was of the lp-π type, similar to structures 1l and 1m, with the water molecule poised above the CF_2 group. There were no minima corresponding to 1n and 1o. The authors also noted a CCl··O halogen-bonded dimer, corresponding closely to 2h. Unlike our aug-cc-pVTZ computations which place the latter higher in energy than the former by 0.37 kcal/mol, the smaller set results in a dead heat, as the two structures are within only 0.05 kcal/mol of one another. Gou et al identified four different H-bonded structures, all higher in energy than the aforementioned minima by 0.6 - 1.1 kcal/mol. In contrast, the larger aug-cc-pVTZ set yields only a single minimum of this type, 0.9 kcal/mol less stable than the global lp-π structure.

So as to undertake a more systematic examination of the effects of basis set choice, the potential energy surface of the $C_2ClF_3\cdots H_2O$ pair was searched thoroughly by both 6-311++G** and aug-cc-pVDZ, and the results compared with aug-cc-pVTZ. Despite the use of the same basis set, our own search with 6-311++G** yielded somewhat different results than Gou et al. [65] Three different minima of the lp-π variety were identified, as were three different halogen-bonded structures; no H-bonded structures were encountered with the 6-311++G** basis set. As a further difference, even though halogen bonds to the F atom were found as minima, their interaction energy became positive, i.e. repulsive, upon counterpoise correction.

An analogous search with the intermediate aug-cc-pVDZ basis led to a total of nine minima. Three of these were common with the 6-311++G** basis but the other six were new. Unlike 6-311++G**, aug-cc-pVDZ yielded no F-bonded minima, a finding in common with aug-cc-pVTZ. Of the nine isomers, four contain a lp-π interaction, one a Cl-bond, and the remaining four isomers contain either OH···Cl or OH···F H-bonds. Summarizing the results above, improving the basis set to aug-cc-pVTZ drops the number of minima to six from nine. The first 5 minima (4 lp-π and 1 halogen bonded) are the same as aug-cc-pVDZ but aug-cc-pVTZ contains only a single H-bonded minimum, combining both OH···F and OH···Cl. On the positive side, although the number of geometries from each of three different basis sets is different, the most stable minimum in all cases is characterized by a lp-π interaction. The binding energy of this configuration gradually becomes more attractive, from 6-311++G** (1.53 kcal/mol) to aug-cc-pVDZ (1.89 kcal/mol) and aug-cc-pVTZ (2.22 kcal/mol). All the geometries obtained by these three basis sets are provided in the supporting information.

This level of sensitivity to basis set is perhaps surprising. Some sensitivity of the electrostatic potential to basis set is expected [84] but consideration of these potentials alone does not resolve these discrepancies. For example, as mentioned above the 6-311++G** basis set indicates the possibility of halogen bonds to the F atoms (see Fig S1). This sort of interaction is usually accompanied by a positive region of potential along the C-X axis. Yet, as is clear from the potentials exhibited for C_2ClF_3 in Fig S4, there is no more of a positive potential in this region for 6-311++G** than for aug-cc-pVDZ and aug-cc-pVTZ, neither of which show any evidence of a F··O halogen bond. As a second point, the smaller basis does not yield any H-bonded OH··X minima. However, this absence cannot be explained by the electrostatic potential which is more negative in the appropriate regions of the C_2ClF_3 molecule. The potentials for the aug-cc-pVDZ and aug-cc-pVTZ basis sets are nearly identical, so again simple Coulombic interactions are incapable of explaining the different minima obtained with these two basis sets.

SUMMARY

The negative electrostatic potential that exists above the molecular plane of a simple alkene molecule would normally repel the negative end of an approaching molecule. However, perhalogenation of the alkene draws electron density away from this π-region, reversing its polarity, thus permitting an electronegative atom to approach from above. As a result, perhalogenated alkenes form complexes with a water molecule in which the O atom rests above the alkene, such that the O lone pairs are able to donate charge into the π* C=C antibonding orbital. These lone pair-π complexes are the most strongly bound dimers formed between water and any of the $C_2F_nCl_{4-n}$ alkenes. An additional factor which adds to their stability is the Coulombic attraction between one of the water protons and the negatively charged halogen atoms; some of these attractions are strong enough to be fairly characterized as a OH··X H-bond. The binding energies of these complexes lie in the narrow range between 2.1 and 2.4 kcal/mol, with only a small dependence upon the number of F atoms n.

A second type of complex in which water and $C_2F_nCl_{4-n}$ engage is a O··Cl halogen bond; F is not a participant in these sorts of interactions. Each such dimer is stabilized by charge transfer from the O lone pairs into the C-Cl σ* antibonding orbital. These dimers are somewhat less stable than the lone pair-π set, with bonding energies in the 1.7 - 1.9 kcal/mol range. The third category of dimer involves a bifurcated H-bond between a water proton and a pair of halogen atoms. These structures are bound by 1.3 - 1.7 kcal/mol.

Within each category above, there is generally more than one particular structure. For example, water can form a halogen bond to each of the three Cl atoms in C_2FCl_3. This same alkene forms three distinct lone pair-π complexes, differing in the particular halogen atom to which the water H atom is attracted. The energy differences between these various isomers are quite small, making a clear determination of the global minimum difficult.

The situation is further complicated when zero point vibrations and entropic effects are included. Indeed, the structure with the most negative value of ΔE is in many cases different from that with the smallest value of ΔG. Whereas the lp-π configurations are the most stable with respect to ΔE and ΔH, followed by halogen and then H-bond, the order is quite different for ΔG. The lowest values of ΔG are associated with halogen bonds, with the other two interactions both somewhat higher. The results are also sensitive to choice of basis set. With all of these issues combined, it would be difficult to establish the single most stable dimer structure from ab initio calculations, even those carried out at a high level.

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Table 1: Energetic (kcal/mol) and geometric parameters of most stable minimum of each system containing lp-π interaction on complex formation with H_2O.

O-π interaction	C_2Cl_4 (1a)	C_2Cl_3F (1c)	$C_2Cl_2F_2$			C_2ClF_3 (1l)	C_2F_4 (1p)
			Cis (1h)	Trans (1i)	gem (1f)		
ΔE	-2.21	-2.27	-2.18	-2.15	-2.44	-2.22	-2.07
R(O···C), Å	3.045	3.028	2.982	3.053	2.832	2.864	2.902
R(H···F), Å	2.813 (Cl)	2.788	2.453	2.989	3.251	3.015	2.816
E(2) $O_{lp}{}^{a}\rightarrow$C-C π*	0.27	0.29	-	0.24	0.89	0.78	0.62
Δq^{b}, me	0.77	0.83	-	0.66	1.70	1.45	1.25
ΔH	-1.87	-1.92	-1.72	-1.50	-1.90	-1.63	-1.44
ΔG	4.41	4.69	4.69	4.29	3.50	4.07	4.44

[a] sum of contributions from two O lone pairs

[b] NBO transfer, defined as $2(F_{ij}/\varepsilon_j - \varepsilon_i)^2$ where F_{ij} refers to Fock matrix element and $\varepsilon_{i/j}$ to donor and acceptor orbital energies

Table 2: Energetic (kcal/mol) and geometric parameters of most stable minimum of each system containing halogen bond on complex formation with H_2O.

Halogen Bond	C_2Cl_4 (2a)	C_2Cl_3F (2b)	$C_2Cl_2F_2$			C_2ClF_3 (2h)
			Cis (2e)	Trans (2f)	Gem (2g)	
ΔE	-1.74	-1.92	-1.91	-1.87	-1.69	-1.85
R(O-Cl), Å	2.978	2.975	2.980	2.981	2.986	2.979
E(2) $O_{lp}{}^{a}\rightarrow$C-Cl σ*	1.07	1.05	1.12	1.05	1.00	1.06
Δq, me	1.37	1.27	1.50	1.27	1.21	1.26
ΔH	-0.83	-0.99	-0.99	-0.94	-0.76	-0.92
ΔG	3.11	3.84	3.27	3.27	2.06	3.76

[a] sum of contributions from two O lone pairs

Table 3: Energetic (kcal/mol) and geometric parameters of most stable minimum of each system containing hydrogen bonds on complex formation with H_2O.

Hydrogen Bond	C_2Cl_4 (3a)	C_2Cl_3F (3b)	$C_2Cl_2F_2$			C_2ClF_3 (3j)
			Cis (3e)	Trans (3f)	Gem (3h)	
ΔE	-1.39	-1.67	-1.65	-1.38	-1.34	-1.31
R(H···Cl)*, Å	2. 806	2.779	2.913	3.118	2.732	2.942
R(H···Cl/F)**, Å	2.759	2.309	2.265	2.211	2.432	2.331
E(2)* Cl → O-H σ*	0.35	0.24	-	-	0.44	0.28
E(2)** F/Cl→ O-H σ*	0.46	0.43	0.58	0.83	0.24	0.38
Δq*, me	0.58	0.30	-	-	0.58	0.35
Δq**, me	0.49	0.46	0.65	0.86	0.27	0.43
ΔH	-0.73	-1.03	-0.96	-0.66	-0.67	-0.59
ΔG	3.73	4.38	4.88	3.39	4.23	5.00

Table 4: SAPT decomposition of total energy of most stable minimum for lp···π interaction, halogen bond and hydrogen bond.

Most stable	lp-π (1f)	Halogen bond (2b)	Hydrogen bond (3b)
ES	-3.74	-2.65	-1.86
EX	3.94	2.58	2.37
IND	-2.07	-1.44	-1.02
IND+EXIND	-0.55	-0.44	-0.41
DISP	-2.96	-1.84	-2.08
DISP+EXDISP	-2.53	-1.60	-1.86
Total	-2.89	-2.11	-1.76

Table 5. Changes within monomers caused by formation of lone pair - π complexes

	C_2Cl_4 (1a)	C_2Cl_3F (1c)	Cis-$C_2Cl_2F_2$ (1h)	Trans-$C_2Cl_2F_2$ (1i)	Gem-$C_2Cl_2F_2$ (1f)	C_2ClF_3 (1l)	C_2F_4 (1p)
Δr(C=C), mÅ	-2.37	-1.24	-1.93	-2.15	-1.60	-1.78	-1.80
Δν(C=C), cm^{-1}	8.0	5.4	5.2	8.6	8.9	8.1	7.5
Δocc(π*, C=C)[a], me	-4.26	-3.21	-3.13	-3.95	-3.54	-3.43	-2.91
Δocc(π, C=C), me	-0.72	-0.83	-0.75	-1.03	-1.11	-1.07	-0.95
Δocc(σ*, C=C), me	-0.34	-0.38	-0.53	-0.58	-0.81	-0.66	-0.69
Δocc(σ, C=C), me	-0.20	-0.14	-0.21	-0.20	-0.06	-0.11	-0.08
Δocc(F/Cl_{lp})[b], me	4.94	3.31	4.38	5.71	6.45	6.45	5.58
Δr(O-H), mÅ	1.94	2.05	1.40	1.59	0.84	0.86	0.87

[a] change in occupation of indicated orbital

[b] Sum of all 12 halogen lone pairs

Table 6. Changes within monomers caused by formation of halogen-bonded complexes

	C_2Cl_4 (2a)	C_2Cl_3F (2b)	Cis-$C_2Cl_2F_2$ (2e)	Trans-$C_2Cl_2F_2$ (2f)	Gem-$C_2Cl_2F_2$ (2g)	C_2ClF_3 (2h)
Δr(C-Cl), mÅ	-2.01	-2.98	-2.29	-3.08	-1.18	-1.98
Δν(C-Cl), cm^{-1}	-0.9	0.2	-0.8	0.1	-0.5	-0.3
Δocc(σ*, C-Cl), me	-0.63	-0.28	0.11	-0.18	-0.48	0.21
Δocc(σ, C-Cl), me	-0.80	-0.60	-0.58	-0.61	-0.59	-0.57
Δocc(F/Cl_{lp})[a], me	9.05	7.61	6.00	6.78	6.99	5.51
Δocc(π*, C-C), me	-0.75	0.29	0.13	0.32	-0.20	0.06
Δocc(π, C-C), me	0.15	0.01	0.06	0.09	0.16	0.18

[a] Sum of all halogen lone pairs except those of atom involved in halogen bond

FIGURE CAPTIONS

Figure 1. Electrostatic potential maps for the isolated $C_2Cl_nF_{4-n}$ monomers. Contours cover the range between +0.01 (blue) and -0.01 (red) au. The surface corresponds to twice the atomic van der Waals radius.

Figure 2. Optimized geometries of $C_2Cl_nF_{4-n}\cdots H_2O$ lp-π complexes for n= 4, 3, and 2. Blue numbers are counterpoise-corrected binding energies in kcal/mol. Distances in Å.

Figure 3. Optimized geometries of $C_2Cl_nF_{4-n}\cdots H_2O$ lp-π complexes for n= 2, 1, and 0. Blue numbers are counterpoise-corrected binding energies in kcal/mol. Distances in Å.

Figure 4. Optimized geometries of $C_2Cl_nF_{4-n}\cdots H_2O$ halogen-bonded complexes. Blue numbers are counterpoise-corrected binding energies in kcal/mol. Distances in Å.

Figure 5. Optimized geometries of $C_2Cl_nF_{4-n}\cdots H_2O$ H-bonded complexes. Blue numbers are counterpoise-corrected binding energies in kcal/mol. Distances in Å.

Figure 6. Electron density shifts resulting from complex formation for most stable a) lp-π, b) halogen bond and c) H-bonded complex. Density increases designated by blue, and loss by red; contours represent ±0.0002 au.