Thermodynamics of Hydrogen Bonding from Molecular Orbital Theory: 2. Organics

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Hartree-Fock theory and density functional theory were used to compute the enthalpy and entropy changes of dimerization for a number of hydrogen-bonding compounds. In Part 1, the calculational methods and procedures use for the water dimer are described, and the results obtained are compared with those of others and with experimental estimates in the literature. Here, a variety of organic compounds that can self associate and/or cross associate are considered. The results obtained for the self-association of these compounds are compared with estimates obtained from various types of experimental data. The results are also used to examine the validity of group-contribution methods for hydrogen-bonding mixtures and to test a simple estimation procedure for cross dimerization that can reduce the number of calculations, such as those described here, that need to be done.

Introduction

In the companion article we considered several methods of *ab initio* molecular orbital calculations for the thermodynamic parameters of hydrogen bonding in water. In these calculations we used both the Hartree–Fock (H–F) (Hartree, 1928a,b; Fock, 1930) theory and density functional theory (DFT) (Parr and Yang, 1989) in the form of Becke's 3-parameter (Becke, 1992a,b, 1993) functional with the gradient correction to the correlation energy of Lee, Yang, and Parr (Lee et al., 1988) (B3LYP). We found that the B3LYP calculations were in excellent agreement with reported geometric parameters and harmonic frequencies for the water monomer and linear dimer, and also with the results of higher-level *ab initio* calculations. The H–F results were also in good agreement with experimental estimates of enthalpy (ΔH) and entropy (ΔS) changes on hydrogen bonding. These methods and calculational procedures used are described in Part 1.

In this article we use both of these calculational methods for other hydrogen-bonding components for several reasons. First, we want to examine the difference in the values of thermodynamic parameters for industrially interesting hydrogen-bonding chemicals obtained from the H–F and more computationally intensive B3LYP methods. Second, we want to obtain values for the hydrogen-bonding parameters (enthalpies, entropies, and equilibrium constants) that we will use in subsequent work to obtain an engineering description of these fluids using, for example, the SAFT (Chapman et al., 1990; Huang and Radosz, 1990) equation of state. Third, we want to examine in a fundamental manner the applicability of mixture group contribution methods such as UNIFAC (Fredenslund et al., 1975; Reid et al., 1987) to hydrogen-bonding compounds. We do this by determining if, from the results we obtain, the enthalpy and entropy changes of a hydrogen bond between functional groups is independent of the molecules on which these groups appear. Finally, to reduce the number of *ab initio* calculations that must be done in the future, we also examine whether one can predict the thermodynamics of cross-dimer formation from information on the formation of pure dimers.

Results

The H–F calculations were performed using the basis set 6-31g(d,p), while the B3LYP calculations were performed using the basis set 6-31+ + $g(2d,p)$. The calculations are for isolated molecules at 298 K and 1 atm. Therefore, we want to emphasize that these results are directly applicable only to the vapor phase of hydrogen-bonding fluids, where dimers are the dominant associated species. All calculations were performed using the Gaussian (Gaussian, Inc., 1993, 1995) suite of computational chemistry programs.

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Pure dimers

Our first calculations were for a set of self-associating dimers. For a component to self-associate, it must possess both a hydrogen-bond donor site and a hydrogen-bond acceptor site. Examples of compounds or classes of compounds that can self-associate are water, primary alcohols, and acids.

We initially considered the water dimer. The configuration where the two molecules form a single bond, or a linear dimer, was discussed in the companion article. We now consider a water dimer with a cyclic geometry in which the two molecules form two bonds. Since our calculations were performed at gas-like conditions (298 K and 1 atm), it was not apparent *a priori* which dimer configuration would be thermodynamically preferred. The results of these calculations are presented in Table 1.

For both methods, the results indicate that the linear dimer is thermodynamically favored over the cyclic dimer, and that this is primarily due to the additional entropic penalty associated with forming multiple bonds between the molecules. The enthalpic results can be understood because forming a cyclic dimer results in poor alignment of the monomeric dipoles, and the formation of two weaker bonds instead of a single, stronger bond in the linear dimer. Also, the cyclic dimer is not a true thermodynamic minimum, as evidenced by the fact that the harmonic frequency calculation produces an imaginary frequency. This is indicative of a transition state, which we believe is related to the interchange of the donor and acceptor molecules in the linear dimer.

The second class of self-associating compounds we studied were the primary alcohols. Previous work by Wu and Sandler (1991), which was concerned with identifying generalizable functional groups in organic compounds, has shown that the primary alcohols can be divided into two subgroups: methanol, and the other primary alcohols. One part of this study was to examine whether this grouping is also appropriate when hydrogen bonding is considered; this will be considered later. To minimize the computational resources required for this study, the largest self-associating dimers involving primary alcohols we examined were those formed by ethanol. We investigated both linear and cyclic dimer structures for the primary alcohols. The linear dimer could be viewed as a precursor structure to higher n-mer formation, while the cyclic dimer is representative of a terminal dimer. The results of these calculations are also presented in Table 1.

We expected that the ΔG of linear dimer formation would be small and positive for the primary alcohols. If ΔG were negative, and if the linear dimer was a good approximation for all higher order association "reactions," this would suggest that a high degree of polymerization exists at gas-phase conditions. If the ΔG were large and positive, there would be no appreciable association, even at liquid densities. We also expected that the enthalpy change of dimerization for ethanol and methanol would be nearly equal, since these two compounds have very similar dipole moments and polarizabilities, and that the ethanol dimer would have a larger (in magnitude) entropy change of dimerization due to increased steric hindrance.

Both calculational methods produced qualitatively correct ΔG values for linear dimers of methanol and ethanol, and show the expected trends for both the enthalpy changes and the entropy changes. As was the case for the linear water dimer, the H–F results predict greater association than do the results of the B3LYP calculations. Both methods indicate that the linear alcohol dimers are thermodynamically favored over the cyclic dimers. The cyclic dimers were predicted to be transition states by both methods.

The final class of self-associating compounds we studied were carboxylic acids. We have performed calculations on only cyclic dimers, as these compounds have been experimentally observed to form only such dimers in the vapor phase. We expected the ΔG of hydrogen bonding for the acid dimers to be negative in order to match the experimental observations of nearly complete vapor-phase dimerization at ambient temperatures. Our results are presented in Table 1.

Both calculational methods produced values for the ΔG of dimerization for all the acids that could lead to significant dimerization at gas-phase densities, in agreement with experimental observations. It is pleasing that in the case of the acids, for which significant dimerization occurs, the two calculational methods are in quantitative agreement.

Comparison with Experiment. The two methods have produced very different predictions for the extent of association for some of the self-associating compounds. We hoped to quantitatively judge the accuracy of each method by comparing the predictions to experimental estimates of the thermodynamic parameters found in the literature. The linear water dimer results were compared to experiment in Part 1. Table 2 presents a comparison for linear methanol dimerization and cyclic acid dimerization.

In the case of methanol dimerization, each of our calculational methods agrees reasonably well with one of the experi-

Table 1. Thermodynamic Properties for Pure Dimers

	H–F				B3LYP			
Compound	ΔH (kcal/mol)	ΔS (cal/mol·K)	ΔG (298 K) (kcal/mol)	K_{eq} (298 K)	ΔH (kcal/mol)	ΔS (cal/mol·K)	ΔG (298 K) (kcal/mol)	K_{eq} (298 K)
H_2O—linear	−3.929	−18.324	1.536	7.480×10^{-2}	−2.993	−21.087	3.294	3.847×10^{-3}
H_2O—cyclic	−4.023	−22.211	2.599	1.240×10^{-2}	−2.755	−23.345	4.205	8.267×10^{-4}
MeOH—linear	−3.877	−19.937	2.067	3.05×10^{-2}	−3.130	−22.379	3.542	2.53×10^{-3}
EtOH—linear	−4.100	−25.111	3.387	3.29×10^{-3}	−3.035	−25.493	4.565	4.50×10^{-4}
MeOH—cyclic	−3.909	−27.030	4.150	9.07×10^{-4}	−2.772	−28.541	5.737	6.22×10^{-5}
EtOH—cyclic	−3.805	−29.831	5.089	1.86×10^{-4}	−2.677	−29.757	6.195	2.87×10^{-5}
HCOOH	−13.557	−34.515	−3.266	248	−13.497	−37.290	−2.379	55.5
CH_3COOH	−13.924	−34.052	−3.771	582	−13.958	−36.097	−3.196	220
C_2H_5COOH	−13.720	−34.311	−3.490	362	−13.742	−37.205	−2.649	87.5

Table 2. Calculated Results vs. Experimental Estimates

Dimer	Quantity	Experimental Estimate	H–F	B3LYP
Linear MeOH	ΔH (423 K, kcal/mol)	−3.3*, −4.3**	−2.40	−2.76
	ΔS (423 K, cal/mol·K)	−16.7*, −24.9**	−15.56	−21.34
	ΔG (423 K, kcal/mol)	3.77*, 6.24**	4.19	6.27
	K_{eq} (423 K)	1.13×10^{-2}, 5.98×10^{-4}	6.85×10^{-3}	5.77×10^{-4}
Cyclic HCOOH	ΔH (300 K, kcal/mol)	−14.8±0.5†, −13.7±0.7† −14.1±1.5§	−13.56	−13.50
	ΔS (300 K, cal/mol·K)	−36.20±2.0†	−34.52	−37.29
Cyclic CH_3COOH	ΔH (300 K, kcal/mol)	−14.6±0.5†, −14.8±1.0† −14.2±0.7§	−13.92	−13.96
	ΔS (300 K, kcal/mol)	−34.8±2.0†	−34.05	−36.10
	ΔH (373 K, kcal/mol)	−14.64±0.8‡	−13.75	−13.85
	ΔS (373 K, cal/mol·K)	−35.50±0.8‡	−33.63	−35.85
Cyclic C_2H_5COOH	ΔH (300 K, kcal/mol)	−14.9±0.6†	−13.72	−13.74
	ΔS (300 K, kcal/mol)	−37.0±2.5†	−34.31	−37.21

*Data of Kell and McLaurin (1969) based on second virial coefficient data.
**Data of Kudchaker and Eubank (1970) based on second virial coefficient data.
†Data of Clague and Bernstein (1969) based on IR spectroscopy.
‡Data of Frurip et al. (1980) based on thermal conductivity data.
§Data of Mathews and Sheets (1969) based on IR spectroscopy with a correction for surface adhesion.

mental estimates. However, the experimental estimates do not agree with each other. This disagreement occurs even though the two estimates are both derived from second virial coefficient data. This demonstrates the difficulty of experimentally determining accurate dimerization parameters for the weakly associating alcohols. Given the large discrepancy between the two experimental estimates, it is not possible to judge which calculational method is more accurate, based solely on the methanol results.

For cyclic acid dimerization, the two methods show excellent agreement with the experimental estimates. The predictions fall within the experimental error bars, except when the reported error bars are especially narrow. It is reassuring that the predictions can match experimental estimates for these well-studied and characterized systems. Again, it is not possible to discriminate between our two calculational methods on the basis of these cyclic acid results.

For a further comparison of the results calculated here with those from experiment, we consider the values of the vapor-phase association constants for methanol, ethanol, formic acid, and acetic acid as reported in the DECHEMA Chemistry Data Series (Gmehling and Onken, 1977). These constants are based on the correlation of mixture vapor–liquid equilibrium data, and are reported as the best-fit coefficients in the equation

$$\ln K_{eq}^{v} = \alpha + \frac{\beta}{T}. \tag{1}$$

We have calculated the equilibrium constants for these substances at temperatures from the triple point to the critical point, and then found the best-fit coefficients for Eq. 1. The results are reported in Table 3, along with the predictions of K_{eq}^{v} (298 K) from the various methods.

Our results for the association constants of the alcohols do not agree well with those given in the DECHEMA data series. While the H–F parameters for methanol give good agreement with the DECHEMA value of K_{eq}^{v} (298 K), the discrepancy between the values of α and β indicate that this agreement will be over a limited temperature range only. One difficulty in comparing our parameters with those from DECHEMA is that the latter were fit to vapor–liquid equilibrium data and such a correlation must account for all the degrees of association that may occur with only an apparent dimerization equilibrium constant, while our results are strictly for linear dimerization. Consequently, the parameters reported in DECHEMA should overestimate the extent of dimerization. A more reliable comparison is for acid dimerization, as the compounds are known to form only monomers and dimers in the vapor phase. In these cases, the parameters from both of our methods are in excellent agreement with those from DECHEMA, as we expect for systems with well-defined associations. This provides a degree of assurance in the validity of our calculations. Incidentally, the results of the simpler H–F calculations are in better agreement with the DECHEMA reported values.

Cross dimers

Carbonyl Compounds. The next category of dimers included in this study were cross dimers of small molecules. The first group considered could be generally described as carbonyl compounds. This group encompasses a number of

Table 3. Calculated Results vs. Estimates from DECHEMA

Dimer	Quantity	DECHEMA	H–F	B3LYP
Linear MeOH	α	−5.562	−9.995	−11.223
	β	884	1,965	1,587
	K_{eq} (298 K)	0.075	0.033	0.0027
Linear EtOH	α	−11.584	−12.599	−12.771
	β	3,028	2,076	1,539
	K_{eq} (298 K)	0.240	3.6×10^{-3}	5×10^{-4}
Cyclic HCOOH	α	−18.103	−16.991	−18.519
	β	7,099	6,702	6,713
	K_{eq} (298 K)	301	244	54.4
Cyclic CH_3COOH	α	−17.362	−17.466	−18.606
	β	7,290	7,112	7,169
	K_{eq} (298 K)	1,200	602	233

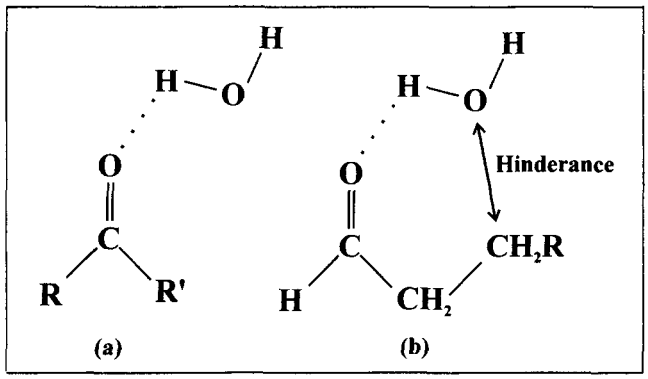

Figure 1. (a) Dimer formed between water and generic carbonyl-containing compound ($R \neq R'$, two possible different dimers); (b) minimum energy configuration of dimers formed by water and butyraldehyde or proprionaldehyde.

The proximity of the second carbon in the chain to the aqueous oxygen results in some steric hindrance and lowers the magnitude of the hydrogen-bonding energy.

small molecules that contain the C = O functionality, including formaldehyde, larger aldehydes, and ketones. In earlier work by Wu and Sandler (1991), it was shown that the C = O functionality could not be considered a single, generalizable functional group. The conclusion they reached was that three different groups were needed to describe this family of compounds: $H_2C=O$ (formaldehyde), $CH_nCH=O$ (aldehydes), and $CH_nCH_{n'}C=O$ (ketones), where n and $n' \in [1, 2, 3]$.

We wanted to investigate whether this group assignment is also valid when hydrogen bonding occurs. Since these compounds do not contain a hydrogen-bonding proton, self-association is not possible. Therefore, we investigated dimers formed with water as shown in Figure 1a. Notice that although the hydrogen bond (=O···H-O) is not linear with respect to the carbonyl double bond, it is nearly linear when one accounts for the position of the lone pairs on the carbonyl oxygen. Also, note that if $R \neq R'$, there are two different dimers, depending on which side of the carbonyl group the hydrogen bond forms.

We first performed calculations to determine the thermodynamic property changes on dimer formation for the smallest representative compound from each category: formaldehyde, acetaldehyde, and acetone. If the carbonyl group were to be considered to be a single hydrogen-bonding group regardless of in which compound it appeared, the ΔH and ΔS values would have to be very similar in these different compounds. Our expectation was that this would not be the case, and that the enthalpy change upon dimerization would increase with increasing dipole moment of the carbonyl compound. Also, we expected that the entropic change of dimerization would increase upon increasing substitution about the carbonyl group, due to greater steric hindrance between water and the side chains.

Table 4 presents the results of our B3LYP and H–F calculations. There are two entries for acetaldehyde due to it being unsymmetric about the carbonyl group. In the thermodynamic description of a mixture of acetaldehyde and water, it would be preferable to use only one value for ΔG of cross dimerization, presumably an average of the values for the two possible cross dimers. The B3LYP results show a large difference between the ΔG values for the two dimers that can form between water and acetaldehyde. This suggests that a larger number of dimers would form with the water nearer to the lone hydrogen, leading us to conclude that the correct average should be only slightly larger in magnitude than 3.078 kcal/mol. With this "effective" ΔG value for acetaldehyde, there is a similarity in the ΔG of hydrogen bonding for all three compounds at 298 K. However, the differences in ΔH and ΔS of hydrogen bonding of these compounds leads us to conclude that these compounds do not behave similarly when forming hydrogen bonds, and hence should not be considered to contain a single, generalizable functional group for hydrogen bonding. Within the H–F results, the two ΔG for acetaldehyde–water dimerization are nearly equal. However, the values of ΔG are not similar for all three compounds. This supports the conclusion that the C = O functionality cannot be considered a single, generalizable functional group in hydrogen bonding.

The results in Table 4 show that both methods lead to the expected trend of an increasing magnitude of the enthalpy change of dimerization with increasing dipole moment of the carbonyl compounds. If one were to use an arithmetic average of the two ΔH values for acetaldehyde, there would be a nearly linear behavior with carbon number in both calculational methods. However, neither method displays a consistent increase in magnitude of ΔS with increasing substitution about the carbonyl group.

Within the two acetaldehyde–water dimers, we expected the dimer with water nearer the $-CH_3$ group would have values of ΔH and ΔS that are larger in magnitude. The larger enthalpic change can be attributed to a better alignment of the molecular dipoles, and the larger entropic change would be caused by increased steric hindrance. These trends are shown in the results of both methods.

Next we examined other compounds from the same family to test if the group definitions of Wu and Sandler (1991) could be extended to hydrogen bonding. The first family considered

Table 4. Thermodynamic Parameters for Cross Dimers of Small Carbonyl Compounds with Water

	H–F				B3LYP			
Compound	ΔH (kcal/mol)	ΔS (cal/mol·K)	ΔG (298 K) (kcal/mol)	K_{eq} (298 K)	ΔH (kcal/mol)	ΔS (cal/mol·K)	ΔG (298 K) (kcal/mol)	K_{eq} (298 K)
Formaldehyde	−3.605	−22.445	3.087	5.46×10^{-3}	−2.758	−19.817	3.150	4.91×10^{-3}
Acetaldehyde—H_2O near H	−4.014	−23.810	3.085	5.46×10^{-3}	−3.349	−21.557	3.078	5.54×10^{-3}
Acetaldehyde—H_2O near CH_3	−4.302	−24.385	2.968	6.67×10^{-3}	−3.597	−24.711	3.771	1.72×10^{-3}
Acetone	−4.623	−23.365	2.343	19.2×10^{-3}	−4.033	−24.300	3.212	4.42×10^{-3}

Table 5. Thermodynamic Parameters for Cross Dimers: Aldehyde and Ketone Families

Aldehyde Family	H–F ΔH (kcal/mol)	H–F ΔS (cal/mol·K)	H–F ΔG (298 K) (kcal/mol)	H–F K_{eq} (298 K)	B3LYP ΔH (kcal/mol)	B3LYP ΔS (cal/mol·K)	B3LYP ΔG (298 K) (kcal/mol)	B3LYP K_{eq} (298 K)
Near H								
Acetaldehyde	−4.014	−23.810	3.085	5.46×10^{-3}	−3.349	−21.557	3.078	5.54×10^{-3}
Propionaldehyde	−3.994	−23.795	3.100	5.34×10^{-3}	−3.382	−20.667	2.779	9.17×10^{-3}
Butyraldehyde	−3.999	−23.815	3.101	5.33×10^{-3}	−3.374	−22.553	3.350	3.50×10^{-3}
Near C-chain								
Acetaldehyde	−4.302	−24.385	2.968	6.67×10^{-3}	−3.597	−24.711	3.771	1.72×10^{-3}
Propionaldehyde	−3.592	−22.407	3.089	5.44×10^{-3}	−3.037	−23.156	3.867	1.46×10^{-3}
Butyraldehyde	−3.621	−22.127	2.976	6.58×10^{-3}	−3.044	−24.238	4.183	0.86×10^{-3}

Ketone Family	H–F ΔH (kcal/mol)	H–F ΔS (cal/mol·K)	H–F ΔG (298 K) (kcal/mol)	H–F K_{eq} (298 K)
Near CH_3				
Acetone	−4.623	−23.365	2.343	19.2×10^{-3}
Butanone	−4.599	−25.393	2.972	6.63×10^{-3}
2-Pentanone	−4.607	−25.721	3.062	5.69×10^{-3}
Near C-chain				
Butanone	−3.892	−24.467	3.403	3.20×10^{-3}
2-Pentanone	−3.916	−24.551	3.404	3.20×10^{-3}
3-Pentanone	−3.893	−23.527	3.041	5.90×10^{-3}

was the aldehydes up to C_4, and these were studied using both calculational methods. The second family was the ketones up to C_5, and these have been examined using the H–F method only. The H–F aldehyde results in Table 5 support the idea that a single association constant can be used for all aldehyde–water hydrogen-bond formation. This is seen in the configuration in which water is closer to the hydrogen side of the carbonyl, as both the enthalpy and entropy changes upon dimerization vary by less than 1%. For the configuration in which water is nearer to the carbon chain the conclusion is less clear, as the results for acetaldehyde are not in agreement with those for propionaldehyde and butyraldehyde, which, however, are in excellent agreement among themselves. In this case, it appears that one must have a chain larger than a single carbon to achieve equivalence. Smaller values for the enthalpic change upon association for propionaldehyde and butyraldehyde may be explained by steric repulsion between the aqueous oxygen and the second carbon in the chain for these larger aldehydes (see Figure 1b). Similar results were obtained from the B3LYP calculations for the aldehydes. However, only in the B3LYP results was the expected trend of the entropy change upon dimerization increasing in magnitude with increasing steric hindrance observed. This is perhaps a result of the fact that a single low harmonic frequency can greatly affect the calculated entropy.

We next examined ketones up to C_5 using the H–F method. The results, also displayed in Table 5, do not provide conclusive proof that the ketone group can be considered to be a single functional group in hydrogen bonding. For the dimers where water is near a $-CH_3$ group, the values of ΔH of association are in good agreement with each other, while the values for ΔS of association are not. This is also true when dimers are formed with the water nearer the extended carbon chain. In both of these cases, the unusual value of the entropy change is obtained when the dimer is formed with a symmetric ketone. This suggests that it may be necessary to view symmetric and unsymmetric ketones as being members of different groups in hydrogen bonding.

Primary Alcohols. We next studied cross-associated dimers formed by primary alcohols and water. We used alcohols as large as 1-butanol with both the H–F and B3LYP methods, and examined configurations in which the alcohols donated the hydrogen, and configurations in which water donated the hydrogen. The atoms that are participating in the hydrogen bond are underlined in the table of our results.

We first examined the two linear cross dimers formed by methanol and water. Since these compounds are very similar, we expect the enthalpy change for cross dimerization to be nearly equal for the two cross dimers, with a value intermediate to those for self-dimerization of water and methanol; the same behavior was expected for the entropy change. Our results are presented in Table 6, along with those for the self-dimerization of water and of methanol.

The H–F method produced values for the enthalpy change of cross dimerization that are nearly equal, and identical within the accuracy of the calculational method to the values for the self-dimerization of water and methanol. The values of the entropy change of dimerization also follow our expectations. The results obtained using the B3LYP method are not as consistent in this regard. The calculated enthalpy changes of cross dimerization are not in agreement with each other, and fall outside the range of values for the two self-dimerizations. The calculated entropy changes are in reasonable agreement with each other, and near the value for methanol self-dimerization.

We next performed calculations to examine the higher primary alcohols. If the higher primary alcohols are to be considered to contain a single, generalizable functional group for hydrogen bonding, it would be necessary for a particular configuration of the groups in different molecules to have similar values for ΔH and for ΔS. Table 6 presents our results for configurations in which water or the alcohol act as the hydro-

Table 6. Thermodynamic Parameters for Cross Dimers Involving Primary Alcohols

	H-F				B3LYP			
Dimer	ΔH (kcal/mol)	ΔS (cal/mol·K)	ΔG (298 K) (kcal/mol)	K_{eq} (298 K)	ΔH (kcal/mol)	ΔS (cal/mol·K)	ΔG (298 K) (kcal/mol)	K_{eq} (298 K)
$\underline{H_2O}$-$H_2\underline{O}$	−3.929	−18.324	1.536	7.48×10^{-2}	−2.993	−21.087	3.294	3.85×10^{-3}
MeO$\underline{H}$-MeO$\underline{H}$	−3.877	−19.937	2.067	3.05×10^{-2}	−3.130	−22.379	3.542	2.53×10^{-3}
EtO$\underline{H}$-EtO$\underline{H}$	−4.100	−25.111	3.387	3.29×10^{-3}	−3.035	−25.493	4.565	4.50×10^{-4}
MeO$\underline{H}$-$H_2\underline{O}$	−3.960	−19.411	1.828	4.57×10^{-2}	−2.852	−22.094	3.735	1.83×10^{-3}
MeO$\underline{H}$-$\underline{H_2}O$	−3.826	−18.367	1.650	6.17×10^{-2}	−3.284	−22.934	3.553	2.49×10^{-3}
EtO$\underline{H}$-$H_2\underline{O}$	−3.885	−19.353	1.885	4.15×10^{-2}	−2.715	−21.873	3.806	1.62×10^{-3}
1-$C_3H_7O\underline{H}$-$H_2\underline{O}$	−3.882	−19.889	2.048	3.15×10^{-2}	−2.713	−21.775	3.779	1.70×10^{-3}
1-$C_4H_9O\underline{H}$-$H_2\underline{O}$	−3.876	−19.910	2.060	3.09×10^{-2}	−2.686	−22.091	3.900	1.38×10^{-3}
EtO$\underline{H}$-$\underline{H_2}O$	−4.181	−23.911	2.948	6.91×10^{-3}	−3.465	−23.914	3.488	2.77×10^{-3}
1-$C_3H_7O\underline{H}$-$\underline{H_2}O$	−4.186	−23.855	2.927	7.15×10^{-3}	−3.518	−24.144	3.681	2.00×10^{-3}
1-$C_4H_9O\underline{H}$-$\underline{H_2}O$	−4.218	−23.919	2.913	7.31×10^{-3}	−3.457	−24.164	3.747	1.79×10^{-3}
EtO$\underline{H}$-MeO$\underline{H}$	−3.809	−19.809	2.097	2.90×10^{-2}	−3.001	−23.164	3.905	1.37×10^{-3}
1-$C_3H_7O\underline{H}$-MeO$\underline{H}$	−3.810	−19.789	2.090	2.94×10^{-2}				
1-$C_4H_9O\underline{H}$-MeO$\underline{H}$	−3.799	−19.771	2.096	2.91×10^{-2}				
EtO$\underline{H}$-MeO$\underline{H}$	−4.173	−25.119	3.316	3.71×10^{-3}	−3.111	−25.416	4.467	0.53×10^{-3}
1-$C_3H_7O\underline{H}$-MeO$\underline{H}$	−4.175	−25.088	3.305	3.78×10^{-3}				
1-$C_4H_9O\underline{H}$-MeO$\underline{H}$	−4.205	−25.147	3.292	3.86×10^{-3}				

gen donor. When the alcohol is the hydrogen donor, the H-F method produces values for the enthalpy and entropy changes of cross dimerization that are identical for the different alcohols to within the accuracy of the calculational method. The results of the B3LYP method lead to the same conclusions. When water is the hydrogen donor, the H-F method again produces values for each of the enthalpy and entropy changes for all the higher alcohols that are identical within the accuracy of the calculational method, as does the B3LYP method. These results support the use of $-C_2H_4OH$ as a generalizable group for hydrogen bonding.

We also considered dimers between methanol and a higher primary alcohol using the H-F method. Configurations in which both the methanol and the higher alcohol donate the hydrogen were studied. These results are also presented in Table 6, and indicate that $-C_2H_4OH$ can be considered a single, generalizable group for hydrogen bonding.

Prediction of Cross-dimer Parameters

A question that arises in the study of systems that can cross associate is if there is a simple method to predict the cross-association parameters. Having performed calculations for a number of cross-associating and self-associating dimers, our results can be used for testing various models. The simplest assumption that can be made about forming a mixed dimer from two compounds that can self-associate is that the cross-association enthalpy and entropy changes are each the algebraic average of the self-associating quantities. That is, if compounds A and B can both self-associate, we assume for the cross-association reaction $A + B \rightarrow AB$ that

$$\Delta H_{AB} = \frac{1}{2}(\Delta H_{AA} + \Delta H_{BB})$$

and

$$\Delta S_{AB} = \frac{1}{2}(\Delta S_{AA} + \Delta S_{BB}). \quad (2)$$

This implies that

$$\Delta G_{AB} = \frac{1}{2}(\Delta G_{AA} + \Delta G_{BB})$$

and that

$$K_{AB} = \sqrt{K_{AA}K_{BB}}. \quad (3)$$

We first tested this assumption by considering linear dimers that involve water and the primary alcohols. The results are given in Table 7 where the atoms that participate in the hydrogen bond are underlined. These results show that, in general, using the algebraic average for the enthalpy and entropy changes is a good assumption for these cross dimers. For the cross dimers involving water, the calculated ΔH values from both methods bracket the values computed from Eq. 2, and in only one case is this not true for the ΔS values. For the alcohol cross dimers, the H-F -calculated results bracket the values from Eq. 2 for both the enthalpy and entropy changes. The B3LYP-calculated enthalpy changes overestimate the predicted value, while the entropy change from Eq. 2 is intermediate to the two calculated values.

While none of the calculated results for the linear dimers agree exactly with the simple approximations of Eqs. 2 and 3, they generally bracket the predictions of Eqs. 2 and 3. This suggests a cancellation of errors since the thermodynamic parameters for the two possible cross dimers would be equal using this simple assumption (i.e., B denotes hydrogen to A is equal to A donates hydrogen to B).

We performed similar calculations for cyclic dimers of a carboxylic acid with water using the H-F and B3LYP methods, and also with methanol at the H-F level. The results are presented in Table 8. In these cases, the correct pure dimers for water and methanol are cyclic. Once again, the algebraic averages of Eq. 2 are nearly equal to the calculated results. Consequently, we conclude that no large errors should ensue in either calculational method by making the assumption of

Table 7. Comparison of Predicted and Calculated Thermodynamic Parameters of Cross Dimers Involving Primary Alcohols

	H-F				B3LYP			
Dimer	ΔH (kcal/mol)	ΔS (cal/mol·K)	ΔG (298 K) (kcal/mol)	K_{eq} (298 K)	ΔH (kcal/mol)	ΔS (cal/mol·K)	ΔG (298 K) (kcal/mol)	K_{eq} (298 K)
MeOH-H_2O	−3.960	−19.411	1.828	4.57×10^{-2}	−2.852	−22.094	3.735	1.83×10^{-3}
MeOH-H_2O	−3.826	−18.367	1.650	6.18×10^{-2}	−3.284	−22.934	3.553	2.49×10^{-3}
Eq. 2	−3.903	−19.131	1.801	4.78×10^{-2}	−3.062	−21.733	3.418	3.12×10^{-3}
EtOH-H_2O	−3.885	−19.353	1.885	4.15×10^{-2}	−2.715	−21.873	3.806	1.62×10^{-3}
EtOH-H_2O	−4.181	−23.911	2.948	6.91×10^{-3}	−3.465	−23.322	3.488	2.77×10^{-3}
Eq. 2	−4.015	−21.718	2.460	1.57×10^{-2}	−3.014	−23.290	3.930	1.32×10^{-3}
MeOH-EtOH	−3.809	−19.809	2.097	2.90×10^{-2}	−3.001	−23.164	3.905	1.37×10^{-3}
MeOH-EtOH	−4.173	−25.119	3.316	3.71×10^{-3}	−3.111	−25.416	4.467	0.53×10^{-3}
Eq. 2	−3.989	−22.524	2.727	1.00×10^{-2}	−3.083	−23.936	4.053	1.07×10^{-3}

Eq. 2, provided one has used the appropriate pure dimers in the calculations.

Conclusions

We used two different calculational methods to estimate the thermodynamic property changes of hydrogen bonding: the computationally inexpensive H-F method, and the more rigorous B3LYP method. The two methods performed equally well qualitatively, as both methods were able to produce accurate results for cyclic pure acid dimers, matching experimental estimates over at least a limited range of temperatures. Both methods produced the expected trends in the values of thermodynamic parameters of hydrogen bonding across the family of carbonyl compounds, and were able to show equivalence of the alcohol group in primary alcohols larger than methanol when involved in hydrogen bonding. These results suggest that it may be possible to use group-contribution methods for these hydrogen-bonding mixtures. Both *ab-initio* methods also showed that for cross dimers of compounds that can self-associate, the algebraic average of the pure-component enthalpy and entropy changes on dimerization is a reasonable estimate for cross dimerization.

The two *ab-initio* methods did not give results that agreed quantitatively for the thermodynamic parameters of dimerization for weakly dimerizing substances, but did for the very important case of the carboxylic acids that exhibit a high degree of cyclic dimerization. In all other cases, the B3LYP method produced values of ΔG that were less favorable for association. However, given the uncertainties in the experimental estimates of the thermodynamic parameters of association, it is not possible for us to determine which method is the more accurate.

There exist several potentially large errors when using the H-F procedure (see the companion article for discussion); however, it appears that with this calculational procedure a consistent cancellation of errors may occur for dimerization calculations leading to reasonably good overall results. We do not know whether this cancellation of errors will occur for clusters larger than dimers. We believe that our results show that H-F calculations may be a relatively inexpensive way to obtain good estimates of the thermodynamic parameters of hydrogen bonding reactions, at least for dimers, and that the additional expense of B3LYP calculations does not produce a noticeable improvement in the calculated results, although theoretically its results should be more accurate.

One of the goals of this work was to improve the description of the phase behavior of hydrogen-bonding fluids. The results of our calculations are applicable to the vapor phase of hydrogen-bonding fluids, but are not directly applicable to the liquid phase. This is because in the liquid phase of associating compounds the thermodynamic properties are governed not by monomer-dimer transitions, but by loose, fluctuating assemblies of larger numbers of molecules. Detailed study of these larger structures at a high level of *ab-initio* theory is a

Table 8. Comparison of Predicted and Calculated Thermodynamic Parameters of Cyclic Cross Dimers Involving Acids

	H-F				B3LYP			
Dimer	ΔH (kcal/mol)	ΔS (cal/mol·K)	ΔG (298 K) (kcal/mol)	K_{eq} (298 K)	ΔH (kcal/mol)	ΔS (cal/mol·K)	ΔG (298 K) (kcal/mol)	K_{eq} (298 K)
HCOOH-H_2O	−8.852	−28.886	−0.240	1.499	−7.556	−30.984	1.682	5.85×10^{-2}
Eqs. 2 and 3	−8.790	−28.363	−0.334	1.757	−8.126	−30.318	0.913	21.4×10^{-2}
HAc-H_2O	−8.735	−28.918	−0.113	1.210	−7.516	−30.869	1.688	5.79×10^{-2}
Eqs. 2 and 3	−8.974	−28.131	−0.587	2.692	−8.357	−29.721	0.504	42.7×10^{-2}
C_2H_5COOH-H_2O	−8.106	−28.972	0.532	0.407	−7.405	−30.606	1.720	5.48×10^{-2}
Eqs. 2 and 3	−8.872	−28.261	−0.446	2.123	−8.249	−30.275	0.777	26.9×10^{-2}
HCOOH-HAc	−13.801	−34.251	−3.589	428	−13.871	−36.833	−2.889	131.2
Eqs. 2 and 3	−13.741	−34.284	−3.519	380	−13.723	−36.694	−2.783	109.7
HCOOH-CH_3OH	−8.825	−29.937	0.101	0.843				
Eqs. 2 and 3	−8.583	−29.855	0.318	0.557				
HAc-CH_3OH	−8.670	−30.046	0.288	0.615				
Eqs. 2 and 3	−8.766	−29.967	0.169	0.752				

formidable task. Other researchers have addressed this problem by incorporating molecular orbital calculations into molecular dynamics (Laasonen et al., 1993) and Monte Carlo (Tuñón et al., 1996) simulations of liquid water. We have chosen to use the results of our dimerization calculation in an equation of state to model the liquid-phase behavior of hydrogen-bonding fluids. Our work will be detailed in a subsequent publication.

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