Solvent Effects on the Relative Energies of Carbonium Ions. Solvation and Internal Rotation for the Allyl Cation in Liquid Hydrogen Fluoride

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Abstract: Monte Carlo simulations for the planar and perpendicular allyl cations in liquid hydrogen fluoride have been carried out in the NPT ensemble at 1 atm and 0 °C. The intermolecular potential functions that describe the solute–solvent interactions have been developed from ab initio molecular orbital calculations with the split valence 4-31G basis set. The two conformers are represented by different charge distributions but the same Lennard-Jones parameters. The solvent-solvent interactions are described by a function of the TIPS form including one Lennard-Jones term and three charged sites for each HF monomer. The present study provides detailed structural and thermodynamic results on the solvation of a localized and delocalized carbonium ion. The solvation of the planar cation occurs primarily through hydrogen bonds, while the perpendicular conformer has HF monomers strongly bound to the formally charged carbon. In addition, insight into the origin of solvent effects on the relative energies of isomeric carbonium ions is obtained. Consistent with traditional notions on ion solvation, the more localized, perpendicular conformer is found to be better solvated, thereby reducing the rotational barrier by ca. 21 ± 6 kcal/mol. This result is also in accord with recent analyses of NMR data for substituted allyl cations under stable ion conditions.

Solvent effects are well-known to have profound influence on reaction rates and even on the structure of molecules.[1] For example, S_N2 reactions are up to 10^{20} times faster in the gas phase than in water, while the unfolding of proteins in nonaqueous media is an obvious illustration of a solvent effect on structure.[2,3] To understand such phenomena it is important to obtain a molecular level knowledge of the solvation of molecules and of its variations along reaction paths. This goal is being approached in our laboratory through theoretical investigations of a wide range of pure liquids and solutions. One part of this program focuses on the solvation of carbonium ions and solvent effects on their relative energies. These topics are the central theme in the present work.

From fundamental electrostatic considerations, as represented by the Born equation, one would expect differences in the solvation energies for carbonium ions.[4] In particular, more delocalized ions should be progressively less well solvated in polar solvents relative to more localized isomers.[4] Nevertheless, considerable experimental evidence has been interpreted as indicating that solvent effects on the relative energies of carbonium ions are generally negligible.[5,6] Most significantly, Arnett and co-workers have shown that heats of ionization for alkyl halides in several superacid solvents and in the gas are linearly correlated and that they also correlate with the free energies of activation for the solvolyses of the compounds in ethanol.[6]

However, the generality of the notion that carbonium ions are immune to solvent effects was challenged by Jorgensen and Munroe on the basis of quantum mechanical studies of carbonium ion–molecule complexes.[7] Specifically, they found significantly weaker interactions between a model solvent molecule, HCl, and delocalized carbonium ions than more localized isomers. The orgin of the effect could be traced to charge delocalization as in the Born equation and for nonclassical (bridged) ions to their relatively high LUMO energies which makes them weaker electrophiles.[7] The initial advantage for the more localized ion was also not found to dissipate in a study of the bridged and bisected ethyl cations with up to five solvent molecules.[7b] Overall, the conclusion was that solvent effects on the relative energies of isomeric carbonium ions should be enhanced by significant variation in charge delocalization for the ions and by increasing nucleophilicity of the counterions and solvent.

For the most part, the experiments have dealt with isomers that are relatively stable such as tertiary species or highly delocalized aryl systems.[5,6,8] In addition, most data have been obtained in nonnucleophilic superacid media. Even so, some differences in solvation (ca. 2–8 kcal/mol) are apparent in comparisons of secondary and tertiary ions, favoring the secondary species as expected.[6,9] Naturally, the reversal of the Baker-Nathan order for alkyl substituent effects in going from the gas phase to solution is also an obvious example of solvent effects on the relative energies of carbonium ions.[10]

The theoretical analyses of the solvation of carbonium ions have been much extended as described in this paper. The original work was clearly limited by the small number of solvent molecules that could be treated quantum mechanically and by neglecting the effects of statistical averaging at normal temperatures.[7] Consequently, the aim of the present work was to perform the first statistical mechanics simulations for carbonium ions in solution. In this manner new levels of detail could be obtained on the solvation of carbonium ions and on the origin of solvent effects on their relative energies.

A particularly extreme case for possible differential solvation was chosen for this initial study; the planar and perpendicular allyl cations in liquid hydrogen fluoride. The charge in the former species is delocalized by resonance while the latter is a charge localized, primary carbonium ion. The choice of solvent follows from the common use of liquid HF as a relatively nonnucleophilic medium for the support of carbonium ions and from the simplicity of the monomer which is computationally advantageous. After this study was initiated, Mayr et al. reported analyses of NMR data that reveal reductions of ca. 10 kcal/mol for the rotational barriers of allyl cations in superacid solvents as compared to the gas phase.[11] This is consistent with the classical position[4,7] and

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provides a reference point for the quantitative results presented in the following.

Statistical Mechanics Calculations

(a) Monte Carlo Simulations. Monte Carlo simulations were executed for the two dilute solutions, each consisting of one allyl cation and 216 HF monomers in the NPT ensemble at 1 atm and 0 °C. Standard procedures were employed, including Metropolis sampling and the use of cubic samples with periodic boundary conditions.[12] The solvent–solvent interactions were truncated with a spherical cutoff at 8 Å on the basis of FF separation. This allows interactions with roughly 70 other HF monomers. New configurations were generated by selecting a monomer, translating it in all three Cartesian directions, and rotating it about a randomly chosen axis. The volume of the systems was changed on every 1000th move, and all intermolecular distances were scaled accordingly.

In view of the low concentration of the solute, a preferential sampling algorithm was implemented to enhance the statistics for the solute and its near neighbors. Specifically, a modified version of Owicki's procedure was employed.[12,13] The probability of attempting to move a solvent molecule was made proportional to $1/(r^2 + c)$, where r is a distance between the solute and the solvent molecule and c is an adjustable parameter. The constant c was set at 60 Å^2 which caused the solvent molecules nearest the solute to be sampled 3–4 times more often than the ones farthest away. The statistics for the solute were also increased by attempting to move the solute every 40th configuration. In addition, the solute–solvent interactions were truncated at a spherical cutoff of 8 Å on the basis of the central carbon to fluorine separation. Last, the ranges for both the solvent and solute moves were chosen to yield acceptance rates of 40–50% for new configurations.

The simulation for the planar allyl cation was initiated from an equilibrated configuration from a previous MC simulation of this system with a different solvent–solvent potential function. Equilibrium was reestablished after 950K configurations and averaging occurred over the following 2000K configurations. The simulation for the perpendicular conformer was performed next and entailed 1000K configurations for equilibration and another 2000K for averaging. All statistical mechanical calculations werre executed on a Harris Corp. H-80 computer in our laboratory.

(b) Intermolecular Potential Functions. Efficient procedures for obtaining quantum mechanical potential functions have been established and were followed in this work for the solute–solvent interactions.[14] Briefly, the interaction energies from split-valence basis set (4-31G) calculations on 290 orientations of the allyl cation–FH complexes were fit to a 12–6–1 potential function (eq 1). The geometries for the complexes were chosen by using the

$$\epsilon_{mn} = \sum_{i}^{\text{on } m} \sum_{j}^{\text{on } n} (q_i q_j e^2/r_{ij} + A_i A_j/r_{ij}^{12} - C_i C_j/r_{ij}^{6}) \qquad (1)$$

iterative energy-distributed random-geometries procedure to guarantee adequate represention of the low-energy regions of the potential surfaces.[14] The choice of basis set is supported by ab initio studies of protonated alkyl fluorides reported previously.[15] In all aspects of this work, the allyl cations were held fixed in their STO-3G optimized geometries[16] and the experimental bond length of 0.917 Å for HF was adopted.[17] The quantum mechanical calculations were carried out with a modified GAUSSIAN/76 program[18] on the CDC/6600 at Purdue University.

Table I. Parameters for the 12–6–1 Potential Functions for the Allyl Cation–FH Complexes Fit to 4-31G Interaction Energies[a]

		Lennard-Jones parameters	
monomer	site	A_i	C_i
HF			
	F	0.33819	−0.42189
	H	0.00000	0.00000
allyl$^+$			
	C	18177	715.16
	H	422.07	378.54

		Coulomb parameters
monomer	site	q_i
HF		
	F	−0.64942
	H	(0.64942)[b]
allyl$^+$		
planar	C_1	(−0.15266)[c]
	C_2	0.021721
	H_3	0.19715
	H_4	0.20642
	H_5	0.24962
perpendicular	C_1	(−0.35070)[c]
	C_2	0.37083
	C_3	0.97306
	H_4	0.17837
	H_5	−0.13228
	H_6	0.064543
	H_7	−0.051909

[a] Units are for q (electrons), A (kcal·Å^{12}/mol)$^{1/2}$, and C (kcal·Å^6/mol)$^{1/2}$. e^2 in eq 1 is 332.17752 kcal·Å/mol. [b] Charge for the hydrogen is $-q_F$. [c] This parameter was obtained by requiring the charges on each allyl monomer to add up to one.

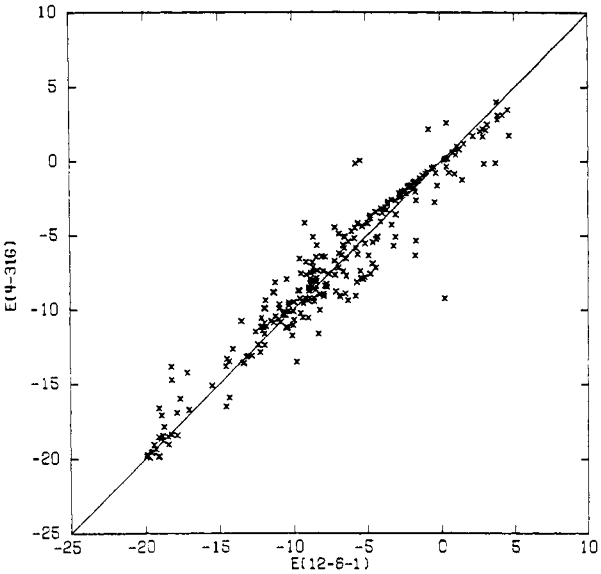

Figure 1. Comparison of interaction energies (kcal/mol) for both conformers of the allyl cation–FH complex from 4-31G calculations and the 12–6–1 potential function.

Since the low energy regions of the potential surface are of primary importance in Monte Carlo simulations, a weighting function was included in the fitting procedure. The weighting function has the form used by Beveridge[19] (see eq 2), where ΔE_0

$$w_i = 1 + \alpha \exp[-(\Delta E_i - \Delta E_0)/kT] \qquad (2)$$

is the minimum interaction energy. In the present case, the ΔE_0s

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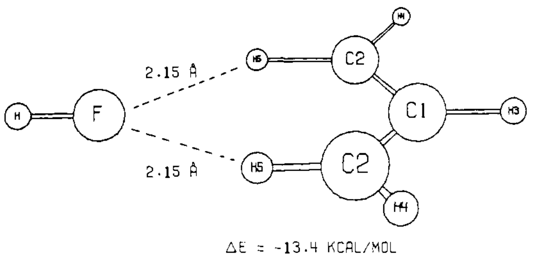

Figure 2. 12–6–1 minium energy configuration for the planar allyl cation–FH complex with C_{2v} symmetry.

of −13.6 and −19.9 kcal/mol were used for the planar and perpendicular conformers and a value of 0.6 kcal/mol was assigned to kT. The parameter α is adjusted to improve the low-energy fit without causing significant deterioration in the high-energy range, An α of 20 was found to be suitable.

Models with 10 interaction sites located on the nuclei were used for both complexes. In order to reduce the number of parameters, the Lennard-Jones parameters for all carbons and hydrogens in the cations were restricted to be identical. In addition, the charges for the allyl cation must sum to +1 e and the HF is neutral to guarantee correct long-range behavior for the potential functions, The optimized Coulomb and Lennard-Jones parameters for the sites are listed in Table I and the 4-31G and 12–6–1 energies (eq 1) are compared in Figure 1. The standard deviations for the fit to the 290 4-31G energies are r_6 (1.69), σ_0 (1.63), σ_{-6} (1.63), and σ_{-12} (1.33), where σ_n refers to the standard deviation in kcal/mol for all points with interaction energies below n kcal/mol. This is an adequate fit considering the depth of the potential wells and the range of calculated energies, It may also be noted that the charge distribution for the HF monomer gives a dipole moment of 2.87 D. This is larger than the experimental gas-phase value of 1.82 D which may reflect the enhanced polarization of the HF molecule in the presence of the cation. However, in general, little significance should be attached to individual parameters obtained in such fitting procedures.[14] There is also little accord between the fit charges and the results of Mulliken population analyses for the allyl cation.[15b]

The potential function for the solvent–solvent interactions was derived empiricly, as reported previously.[20] Numerous Monte Carlo simulations were carried out to determine a function that would yield good thermodynamic and structural results for liquid HF and that would simultaneously provide a reasonable description of gas–phase dimers. The HF monomer is represented by three interaction sites, two on the nuclei and the third at a position 0,166 Å from the fluorine along the FH axis. The charges on the nuclei are $+q$ and on the third site $-2q$ to preserve neutrality. In addition, a single Lennard-Jones term acts between the fluorines. The values of the parameters are 0.725 for q, 3.0 × 10^5 kcal $Å^{12}$/mol for A_{FF}^2, and 425 kcal $Å^6$/mol for C_{FF}^2, while e^2 in eq 1 is 332.18 kcal Å/mol in consistent units. This function was shown to yield an average error of 3% for the energy and density for liquid HF over a 70 °C temperature range at 1 atm.[20]

Results and Discussion

(a) Energy Minima for the Complexes. In the course of exploring the potential energy surfaces for the allyl cation–FH complexes, optimizations were performed to locate the lowest energy structures. For the planar cation, a suprising result was obtained; both the 4-31G calculations and the potential function predict the doubly hydrogen-bonded form with C_{2v} symmetry shown in Figure 2 to be the global energy minimum. The computed ion–FH interaction energies, ΔE_s, are 13.6 (4-31G) and 13.4 (12–6–1) kcal/mol as summarized in Table II. However, the potential surface near the planar ion is quite flat. In particular, there is another minimum with the fluorine above the plane of the ion interacting with a terminal carbon and its two hydrogens. The ΔE_s in this case is 11.2 from the 4-31G calculation and 11.9 kcal/mol with the 12–6–1 function.

Table II. Optimized Total Energies and Interaction Energies for the Allyl Cation–FH Complexes[a]

species	total energy, au	ΔE_s, kcal/mol 12–6–1	ΔE_s, kcal/mol 4-31G
planar (C_{2v})	−215.93404	13.4	13.6
perp (syn)	−215.88832	19.9	19.9

[a] ΔE_s is the energy change for $R^+\cdots FH \rightarrow R^+ + FH$.

Table III. Optimized Distances and Angles for the Allyl Cation–FH Complexes[a]

conformer	symmetry	parameter	12-6-1	4-31G
planar	C_{2v}	R(C1–F)	3.577	3.566
perpendicular	C_s	R(C3–F)	2.123	2.140
		∠CCF	107.3	103.0
		∠CFH	168.6	150.0

[a] Bond lengths in Å; bond angles in degrees. Numbering of carbons is shown in Figures 2 and 3.

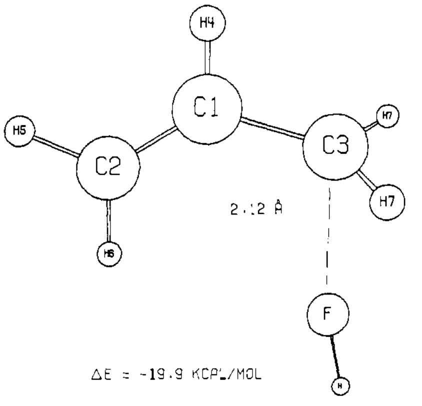

Figure 3. 12–6–1 minimum energy configuration for the perpendicular allyl cation–FH complex (syn).

For the perpendicular conformer, the 4-31G calculations and the potential function find the expected minima with the fluorine interacting directly with the formally charged carbon. The global minimum has the syn structure illustrated in Figure 3 with an interaction energy of 19.9 kcal/mol from both the 4-31G and 12–6–1 calculations. The anti alternative is also a minimum and has ΔE_s values of 19.1 (4-31G) and 19.4 (12–6–1) kcal/mol. The energetic and geometrical results for the global minima are summarized in Tables II and III. The accord between the predictions from the ab initio calculations and the potential function is shown to be excellent. A key point is that in the presence of one HF molecule the quantum mechanical results predict the rotational barrier for the allyl cation to be lowered by 6.3 kcal/mol.

It should be noted that the computed interaction energies are consistent with theoretical and experimental results for protonated alkyl fluorides.[15] In particular, Beauchamp et al. obtained ΔE_s values of 36 and 13 kcal/mol for methyl and ethyl fluoride from ICR measurements.[21] Furthermore, with complete geometry optimization the 4-31G results for the ΔE_s's of methyl, ethyl, and isopropyl fluoride are 29.0, 19.6, and 14.6 kcal/mol, respectively.[15] The similarity of the computed results for the perpendicular allyl and ethyl cations is reasonable since they are both primary ions. In addition, it is often noted that the stability of planar allyl cation is comparable to that of a secondary carbonium ion.[22] Thus, the similarity of the ΔE_s values for the planar allyl and isopropyl cations is interesting. However, the geometries for the complexes are very different, the doubly hydrogen bonded form being preferred for allyl, while the fluorine is near the central cabon for the isopropyl cation.[15b]

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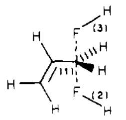
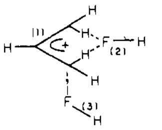
Table IV. Interaction Energies for the Allyl Cations Solvated by Two HF Monomers[a]

				
	perpendicular		planar	
energy	4-31G	12-6-1	4-31G	12-6-1
ΔE_{12}	−19.9	−19.1	−13.2	−13.2
ΔE_{13}	−18.8	−18.8	−11.2	−10.5
ΔE_{23}	0.9	0.6	1.3	0.8
ΔE(total)	−37.8	−37.3	−23.1	−22.9
ΔE_{123}	−35.5		−22.4	
diff	2.3		0.7	

[a] Energies are in kcal/mol.

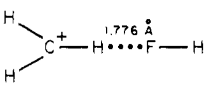
Table V. Thermodynamic Results for the Allyl Cations in Liquid Hydrogen Fluoride at 0 °C and 1 atm[a]

properties	planar cation	perpendicular cation
E_{sx}	−217 ± 1	−242 ± 1
E_{ss}	−1356 ± 2	−1352 ± 2
E_{ss}*	−1410 ± 1	−1410 ± 1
ΔE_{ss}	54 ± 3	58 ± 3
ΔE_{sol}	−163 ± 3	−184 ± 3
V	6445 ± 32	6482 ± 28
V*	6998 ± 18	6998 ± 18
ΔV_{sol}	−553 ± 50	−516 ± 46
ΔH_{sol}	−163 ± 3	−184 ± 3

[a] Calculated results are total quantities for the cation and 216 hydrogen fluoride monomers. E and H are in kcal/mol; V is in Å^3. Subscripts ss and sx indicate the solvent–solvent and solvent–solute contributions. Superscript * indicates the pure solvent. Error bars (±1σ) for the computed quantities were estimated from separate averages over blocks of 50K configurations.

A potential problem in these simulations concerns the neglect of many-body effects. For hydrogen-bonded liquids, it is well-known that cooperative effects can be substantial.[14,20,23] In fact, theoretical studies indicate that three-body effects may account for as much as 15% of the total intermolecular energy in liquids such as water, methanol, and ammonia.[14,23] Nevertheless, little progress has been made on incorporating such effects explicitly in simulations due to their complexity. In view of the even stronger interactions for ion–molecule complexes, it was of interest to obtain estimates of three-body effects for the allyl cation–FH systems. Consequently, some ab initio results on the allyl cations plus two HF monomers were obtained as reported in Table IV. The solvent molecules were placed near the minima discussed above. In the table, the sum of the three individual interaction energies is ΔE(total), while ΔE_{123} is the 4-31G energy difference for the complete complexes less the separated components. In both cases the three-body effect is net repulsive and the magnitude is small (3–7%). However, additional monomers may have a cumulative effect and other geometries may show larger differences. These limited results also indicate that the rotational barrier for the allyl cation may be reduced by ca. 13 kcal/mol in the presence of two HF molecules.

The importance of hydrogen bonding for the planar cation–FH complex was not entirely unexpected in view of previous results.[7,15] In order to provide a basic reference, geometry optimizations at the 4-31G level were performed on hydrogen-bonding arrangements of methyl cation and HF. As with previous calculations for HCl complexes,[7d] the 4-31G optimized geometry of methyl cation and the experimental HF geometry were held constant in each optimization. The global minimum for the hydrogen-bonding configuration of $CH_3^+\cdots FH$ is linear with a ΔE_s of 15.8 kcal/mol (**1**). This value sets an upper bound for hydrogen-bonding interactions between HF and alkyl carbonium ions that is over half the 4-31G dissociation energy of protonated methyl fluoride (ΔE_s = 29.0 kcal/mol).[15b] The cyclic structure (**2**) has a lower ΔE_s of 14.5 kcal/mol. It should be emphasized that the potential surface is very flat for changes in the CHF and HFH angles for structure **1**. The ΔE_s decreases only slightly (0.1 kcal/mol) by varying the angles 15°.



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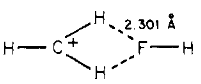

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(b) Thermodynamics and Energy Distributions. The dilute-solution simulations provide thermodynamic data on the process of transferring the allyl cations from the ideal gas phase into liquid HF. In particular, the energy and enthalpy differences, ΔE_{sol} and ΔH_{sol}, are determined from eq 3–7. E_{ss} and E_{sx} are the solvent–solvent and solvent–solute contributions to the total energy of the solution, while E_{ss}* and V* are the reference energy and volume for the pure solvent. The ΔE_{ss} is referred to as the solvent reorganization energy (eq 4). Thus, the energy of solution can be partitioned into two components, the solute–solvent and the solvent disruption terms, as in eq 5. Furthermore, the difference in volume between the solution and the pure solvent gives the volume of solution, ΔV_{sol} (eq 6). Last, the enthalpy of solution is related to the ΔE_{sol} via eq 7, where the PV term for the solute in the gas phase is assumed to be $\approx RT$.

$$\Delta E_{sol} = E_{ss} + E_{sx} - E_{ss}^* \tag{3}$$

$$\Delta E_{ss} = E_{ss} - E_{ss}^* \tag{4}$$

$$\Delta E_{sol} = E_{sx} + \Delta E_{ss} \tag{5}$$

$$\Delta V_{sol} = V - V^* \tag{6}$$

$$\Delta H_{sol} = \Delta E_{sol} + P\Delta V_{sol} - RT \tag{7}$$

The thermodynamic results are compiled in Table V. The computed solvent–solvent energies include cutoff corrections for the Lennard–Jones interactions. As discussed elsewhere, corrections for the Coulombic interactions should be small on the basis of size dependence of the results for liquid HF.[20] The error bars (±σ) are obtained from separate averages over increments of 50K configurations. They may underestimate the true uncertainties by a factor of ca. 2.[24]

As expected, the perpendicular isomer has more attractive interactions with the solvent(E_{sx}) which is accompanied by slightly larger solvent disruption (ΔE_{ss}) than for the planar cation. However, as usual,[12,24,25] the solute–solvent term dominates and the heat of solution is predicted to be 21 ± 6 kcal/mol more exothermic for the perpendicular conformer. This is in good accord with the analyses of NMR data by Mayr et al.[11] They estimated the rotational barrier for the allyl cation to be reduced from about 34 kcal/mol in the gas phase to roughly 24 kcal/mol in superacid solvents.[11] Thus, the relative energetic results in Table V are reasonable. However, experimental data are not available for the absolute heats of solution of carbonium ions in superacid solvents.[6] Obtaining such data reliably is difficult due to effects from ion pairing, the formation of complex counterions, and the need to separate the contributions from the cation and anion.[6] Nevertheless, some related data may be mentioned. The heat of hydration for the *tert*-butyl cation has been estimated from thermodynamic analyses to be ca. −60 kcal/mol.[26] Also, Staley et

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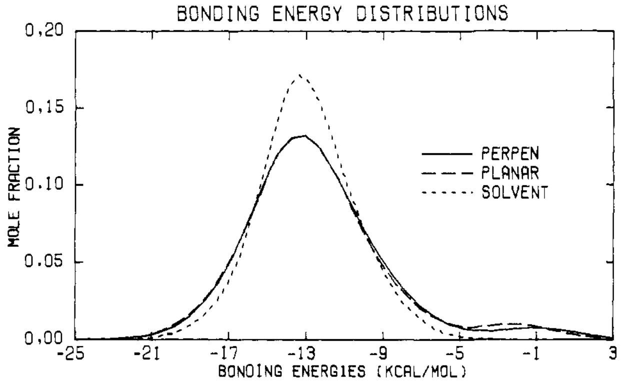

Figure 4. Solvent-solvent bonding energy distributions for solutions of the planar and perpendicular allyl cations and for pure HF. Units for the ordinate are mol fraction per kcal/mol.

al. estimated the combined heats of solution for a series of carbonium ions plus bromide ion in HSO_3F to be −150 to −190 kcal/mol.[27] For reference, the heats of hydration (in kcal/mol) for the following ions may also be noted; Li^+ (−130), Na^+ (−102), K^+ (−82), and Br^- (−75).[28] It seems that the weaker nucleophilicity of HF than water should lead to less exothermic heats of solutions in liquid HF; however, it should be realized that the dielectric constants and dipole moments for the two substances are nearly identical. Furthermore, the solvent disruption term contributes significantly to the heat of solution and somewhat offsets differences in the ion–solvent interactions.[12,24,25] This is strikingly apparent in the small heats of transfer, ca. within ± 10 kcal/mol, for a variety of small cations and anions in going from water to a range protic and dipolar aprotic solvents.[24,29]

All things considered, it is likely that the computed heats of solution for the allyl cations are overly exothermic. This is a general pattern in such simulations of ionic systems that results from the neglect of explicit three-body effects and of polarization of the solvent monomers.[12,24,25] These problems may lead to overestimation of the ion–solvent attraction and underestimation of the solvent disruption. In thee present case, the error is probably also reflected in the significantly negative volumes of solution, ca, −500 Å^3, calculated for the allyl cation. It should be noted that the statistical uncertainty for ΔV_{sol} is significant since the difference of two large numbers is being taken; the convergence of ΔV_{sol} also warrants further study. Along these lines, the results of simulations for the allyl cations with an earlier version of the solvent–solvent potential deserve mention, The computed heats of solution were −132 and −141 kcal/mol for the planar and perpendicular ions and the volumes of solution were only around −85 Å^3. Overall, the important point is that the relative heats of solution are correct, though the possible overestimation of the solute–solvent attraction for both ions should be kept in mind in the analyses of the results which follow.

The distributions of the total solvent–solvent bonding energies for HF monomers in the solutions and in the pure solvent are compared in Figure 4. Three significant features are observed. First, the distributions for the solutions are broader, indicating that HF monomers in the dilute solutions experience a greater range of energetic environments, Second, all three distributions have the principal maximum at about −13 kcal/mol, suggesting that the majority of solvent–solvent interactions are similar in the dilute solutions and in the pure solvent. Last, consistent with earlier studies with hydrogen-bonding solvents,[24,25c] the solutions have a minor peak toward the higher energies due to the repulsive solvent–solvent interactions within the first solvent shell. The small band near −1 kcal/mol integrates to 5.8 monomers for the solutions of both the planar and perpendicular conformers.

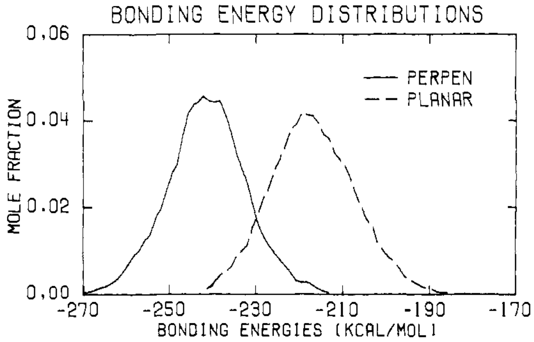

Figure 5. Solvent–solute bonding energy distributions for solutions of the planar and perpendicular allyl cations. Units for the ordinate are mol fraction per kcal/mol.

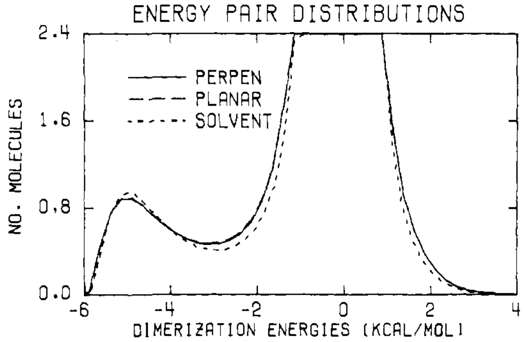

Figure 6. Solvent-solvent energy pair distributions for solutions of the planar and perpendicular allyl cations and for pure liquid HF. Units for the ordinate are number of molecules per kcal/mol.

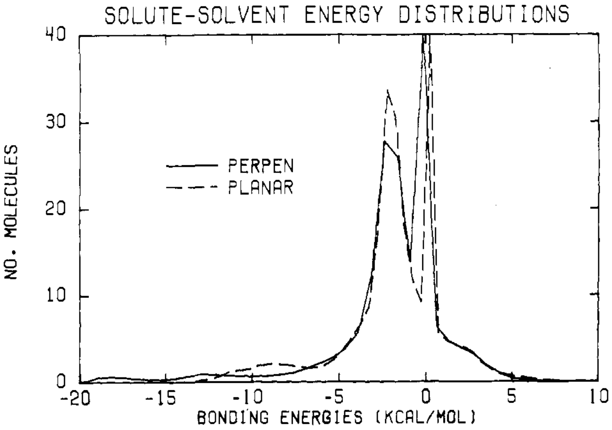

Figure 7. Solvent–solute energy pair distributions for solutions of the planar and perpendicular allyl cations.

The total solute–solvent interaction energies for the planar and perpendicular cation are displayed in Figure 5. Both distributions are unimodal with a range of about 50 kcal/mol. Note that the average of the distributions is E_{sx}. The more attractive solute–solvent interactions for the perpendicular ion are clearly apparent.

The distribution of dimerization energies that an HF monomer experiences in the solutions is similar to that in the pure solvent as illustrated in Figure 6. The distributions consist of two peaks representing the attractions to the hydrogen-bonded neighbors and the weak interactions with the more distant monomers. It is again apparent that the solvent–solvent energetics are not grossly affected by the presence of the solutes.

The multiple maxima in the energy pair distributions for the ion–solvent interactions, shown in Figure 7, indicate there are several energetic environments for solvent molecules around the cations. For the planar allyl ion, the first peak located between −13.0 and −7.0 kcal/mol encompasses 9 HF monomers that are the most bound to the ion. The second peak in the range from −7.0 to 0.0 kcal/mol is centered at −3 kcal/mol and integrates

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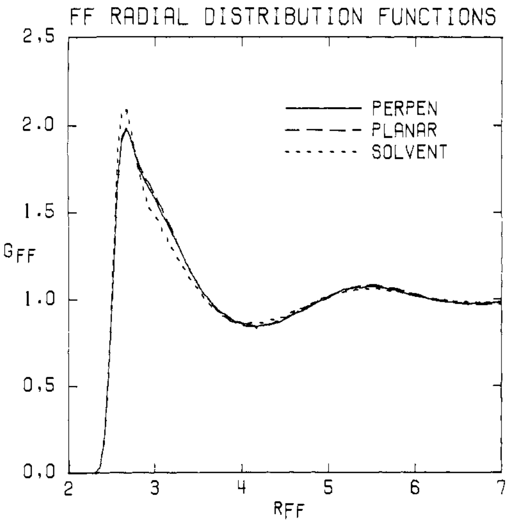

Figure 8. Fluorine–fluorine radial distribution functions for the solutions of the planar and perpendicular allyl cations and for pure liquid HF.

Table VI. Location of Extrema and Coordination Numbers for the Solute–Solvent rdfs for the Planar Allyl Cation[a]

rdf	peak	r(max)	r(min)	coord no.
C1–F	first	3.302	4.654	11.4
C1–F	second	6.682	7.670	57.5
C2–F	first	2.938	4.238	7.9
C2–F	second	5.538	6.630	36.4
H3–F	first	2.626	3.510	3.5
H4–F	first	2.366	3.458	4.1
H5–F	first	2.210	3.458	4.3
C1–H*	first	4.810	5.486	15.1
C2–H*	first	3.822	4.446	6.4
H3–H*	first	3.354	3.822	2.7
H4–H*	first	3.094	3.978	3.3
H5–H*	first	3.042	3.614	2.8

[a] Maxima and minima are in Å and the coordination number is obtained by integrating the rdf to the minimum.

to 74 monomers. The third peak integrates to 120 monomers and represents the interactions of the solute with distant solvent monomers. The shoulder on the high-energy side of this peak represents repulsive interactions between the ion and 13 monomers. These monomers are probably relatively near the ion but maximizing solvent–solvent interactions.

The first peak for the perpendicular allyl cation from −20.0 to −15.0 kcal/mol integrates to 2 monomers which are strongly coordinated to the formally charged carbon as discussed further below. The second peak from −15.0 to −10.0 kcal/mol integrates to 3.4 monomers and may be assigned to other strong solute–solvent interactions close to the ion. The third, fourth, and fifth peaks with energy ranges of −10.0 to −1.0, −1.0 to 1.0, and 1.0 to 10.0 kcal/mol integrate to 69, 127, and 14 monomers, respectively. The interactions for these last three peaks appear similar to those for the planar cation in the same energy regions. Both ions have numerous mildly attractive interactions with solvent molecules through hydrogen bonds or at longer range, through general ion–dipole interactions.

(c) Radial Distribution Functions. The fluorine–fluorine radial distribution functions (rdfs) between solvent molecules for the solutions and pure solvent are compared in Figure 8. The results are also similar for the FH and HH rdfs, again showing no gross disruption of the solvent. As presented previously, the solvent structure is dominated by winding hydrogen-bonded chains with an average of nearly two hydrogen bonds per monomer.[20]

The solute–solvent rdfs for the planar allyl cation will be discussed first. With five unique atoms for the solute and two for the solvent monomer, 10 rdfs are possible. The location of the maxima and minima and the coordination numbers for the major peaks in the rdfs are listed in Table VI. The C–F rdfs are displayed in Figure 9. From the locations of the first peaks it is apparent that there are closer contacts between HF monomers and the terminal carbons then the central carbon.

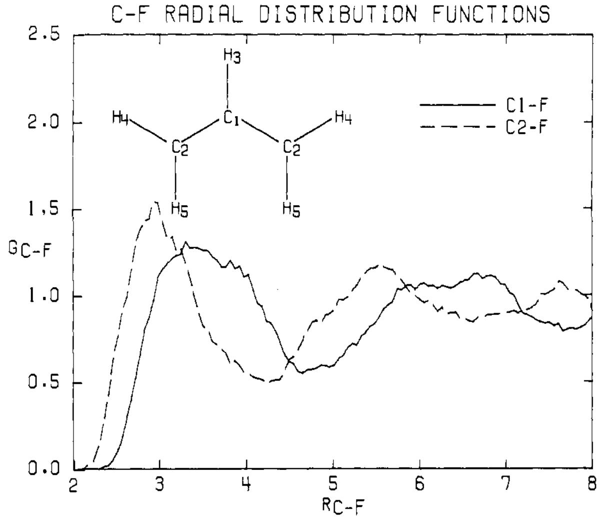

Figure 9. C–F radial distribution functions for the planar allyl cation in liquid HF.

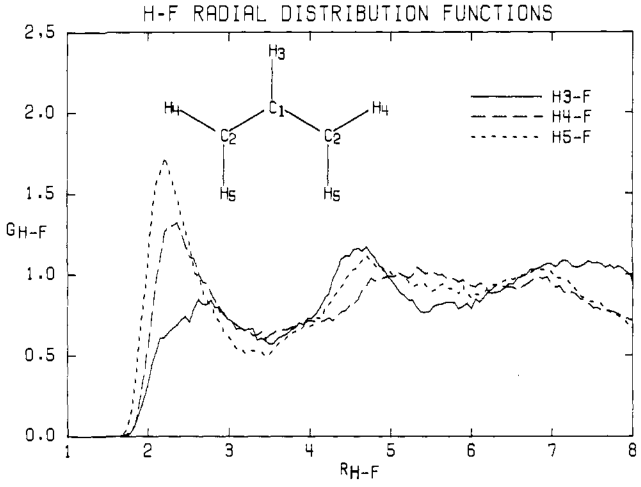

Figure 10. H–F radial distribution functions for the planar allyl cation in liquid HF.

The three H–F rdfs are illustrated in Figure 10. The shortest contacts and strongest first peak are for the interactions of the fluorines with the two inside hydrogens (H5) on the terminal carbons. This is reasonable since the solute–solvent potential function and the 4-31G calculations found the double-hydrogen-bonding artrangement with these hydrogens to be the global energy minimum. The structure in the rdf for H4 is comparable which is also consistent with the favorable hydrogen bonding to this site simultaneously with H5. Interactions with H3 are less favorable as witnessed by the weak first peak. The stronger second peak near 4.8 Å can be attributed to the HF monomers nearer the H4 and H5 atoms.

The rdfs involving the hydrogen of the HF monomers are similar, though less intense than those for the fluorine. Comparison of the locations of the first peaks in the rdfs (Table VI) clearly reveals that the fluorines are nearest the ion and the hydrogens are pointing away. The limited structure in the rdfs for the hydrogens of the solvent indicates significant orientational freedom for the hydrogens. This permits better solvent–solvent hydrogen bonding and helps minimize the solvent disruption.

The seven different atoms for the perpendicular isomer provide 14 rdfs. Only 10 were computed; the H–H* distributions were excluded. The locations of the extrema and the coordination numbers are compiled in Table VII.

The three C–F rdfs are displayed in Figure 11. Significantly greater structure is apparent than in the rdfs for the planar form. The C3–F rdf is particularly interesting with a very sharp first

Table VII. Location of Extrema and Coordination Numbers for the Solute-Solvent rdfs for the Perpendicular Allyl Cation[a]

rdf	peak	r(max)	r(min)	coord no.
C1-F	first	2.730	3.666	5.3
C2-F	first	2.730	3.666	4.6
C3-F	first	2.158	2.470	2.1
C3-F	second	2.678	3.822	6.7
H4-F	first	2.470	3.146	2.9
H5-F	first	3.822	4.446	8.4
H6-F	first	2.366	3.302	3.6
H7-F	first	2.262	3.302	15
C1-H*	first	3.666	4.394	5.6
C2-H*	first	3.562	4.498	6.0
C3-H*	first	3.042	3.250	2.7
C3-H*	second	3.458	4.446	5.4

[a] Maxima and minima are in Å, and the coordination number is obtained by integrating the rdf to the minimum.

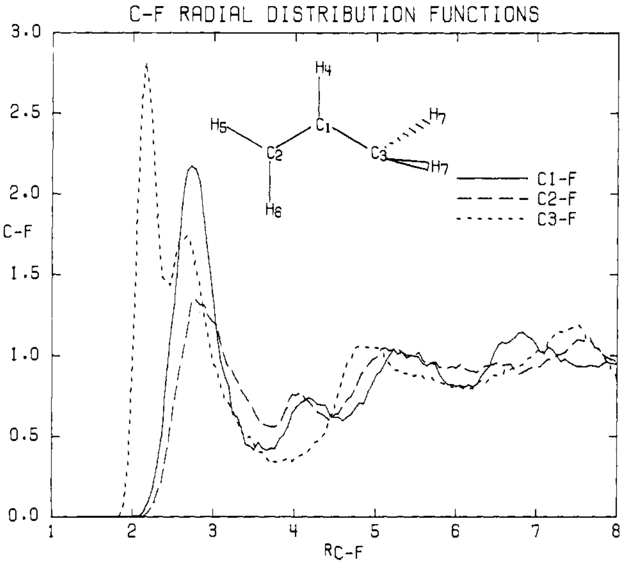

Figure 11. C-F radial distribution functions for the perpendicular allyl cation in liquid HF.

peak. Integration to the first minimum reveals 2.1 neighbors; this is consistent with an HF monomer on both sides of the formally charged carbon (C3) as expected from the minima in the potential function and 4-31G calculations. Integration of the remainder of the band out to 3.8 Å yields another 4.6 HF monomers. These may be hydrogen bonded to the hydrogens (H7) on the carbonium center. It is apparent that the strong solute-solvent interactions are also showing up in the Cl-F rdf. Some of the molecules in the first peak are undoubtedly closer to C3, The C2 atom is farthest away from the carbonium site and, consequently, the least structure is observed in the C2-F rdf.

The H-F rdfs are illustrated in Figure 12. The patterns are consistent with the analyses above, In particular, the sharpest first peak is for the hydrogens (H7) on C3. Integration reveals 15 solvent molecules within 3.3 Å. This undoubtedly includes HF monomers hydrogen bonded to both H7's as well as the monomers coordinated to C3. As before, the structure in the rdfs decreases for the solute hydrogens as their distance from the carbonium carbon increases. The C-H rdfs (not shown) mirror the C-F distributions with reduced structure. The double first peak for the rdf with C3 is again striking. Integration to the minimum at 3.25 Å reveals 2.7 hydrogens, two of which arre readily assigned to the strongly bound HF monomers on C3. Comparison of the locations of the first peaks in the C-F and C-H* rdfs confirms the expected orientation with the fluorines directed toward the ion.

In summary, the variation in structure of the solute-solvent rdfs for the planar and perpendicular allyl cations is pronounced. More structure is apparent for the perpendicular conformer which has two strongly bound HF monomers on the formally charged carbon. For both ions, the solvent is progressively less structured around the atoms of the solute as they are less charged and farther from the carbonium carbons. Hydrogen bonding between the solvent and the hydrogens in the ions is also widespread.

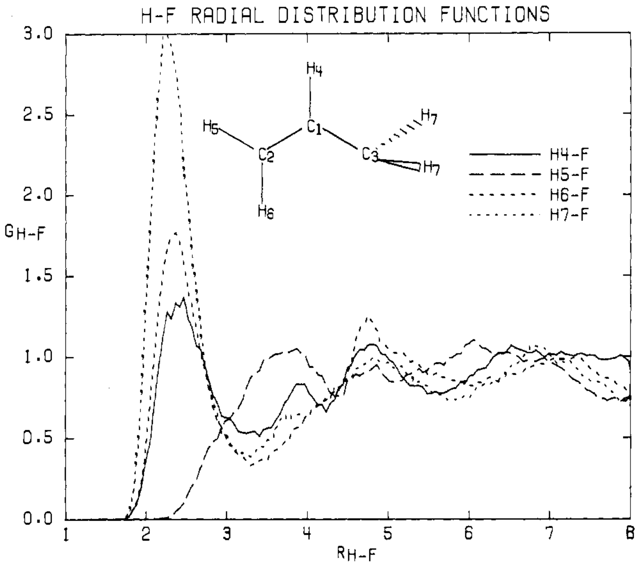

Figure 12. H-F radial distribution functions for the perpendicular allyl cation in liquid HF.

The structure of the solutions can be further elucidated by stereoplots of configurations from the Monte Carlo runs. Examples are provided for the two ions in Figure 13. For clarity, solvent molecules more than 3 Å in front of the solute as viewed have been removed. Thus, only about 160 of the 216 HF monomers are displayed,

For the planar ion, the ion-solvent hydrogen bonding is clearly evident, while direct coordination to the terminal carbons from above and below the molecular plane is not so obvious. It should be realized that this is only one of 2×10^6 configurations, though it is quite typical. The figure reveals the ready accommodation of the hydrogens of the solvent molecules nearest the ions into the hydrogen-bonded chains that are ubiquitous in the solvent. Thus, the disruption of the solvent is minimized. In addition, the stereoplot for the planar conformer nicely shows an HF monomer in the doubly hydrogen-bonded arrangement with the inside hydrogens on the terminal carbons. Furthermore, it appears that the average number of solvent-solvent hydrogen bonds per HF monomer in the first solvent shell is 1 and increases to 2 in the outer regions.

The perpendicular conformer has two HF monomers that are directly coordinated with the formally charged carbon (C3) as well illustrated in the bottom stereoplot. Hydrogen bonding to this end of the ion is also pronounced, while solvation of the other terminal carbon is much diminished. Once again, the hydrogens of the HF monomers nearest the ion are able to align themselves for favorable interactions with solvent molecules in the outer layers. Overall, the structural information from the stereoplots is consistent with and enhances the picture obtained from the energy and radial distribution functions.

(d) Hydrogen-Bonding Analysis. By analysis of configurations saved at regular intervals during the simulations, additional information on the solvent-solvent hydrogen bonding was obtained. The same energetic definition of a hydrogen bond was used as for the pure solvent.[20] It is based on the location of the minimum in the solvent-solvent energy pair distribution (-3.125 kcal/mol) such that any pair of solvent molecules bound by more than this amount is considered to be hydrogen bonded. The resultant distributions of hydrogen bonds for the solutions and pure solvent are similar, as shown in Figure 14. Though the average number of hydrogen bonds is identical in each case, there is a somewhat greater fraction of monomers in two hydrogen bonds in the pure solvent and more in one and three in the solutions. Thus, the presence of the ions makes the chains a little shorter and more

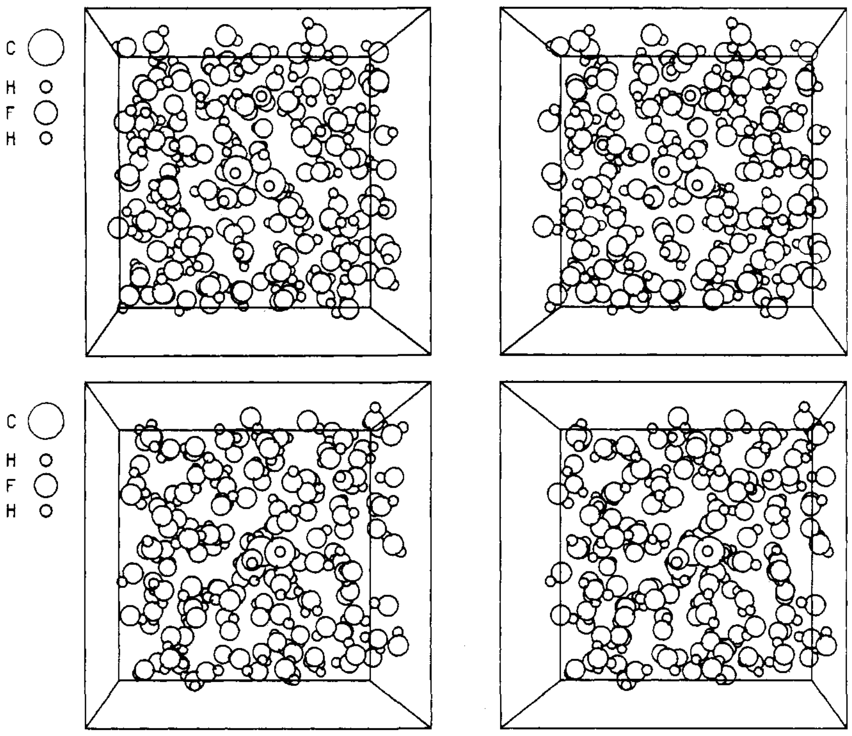

Figure 13. Stereoplots of configurations from the simulations of the planar (top) and perpendicular (bottom) conformers of allyl cation in liquid HF. Hydrogen fluoride molecules more than 3 Å in front of the solute have been removed for clarity.

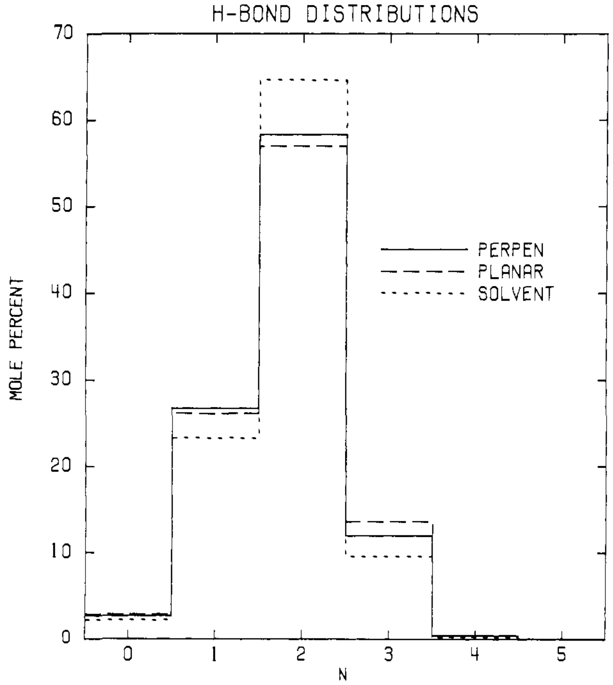

Figure 14. Hydrogen-bond distributions for solutions of the planar and perpendicular allyl cations and for pure liquid HF.

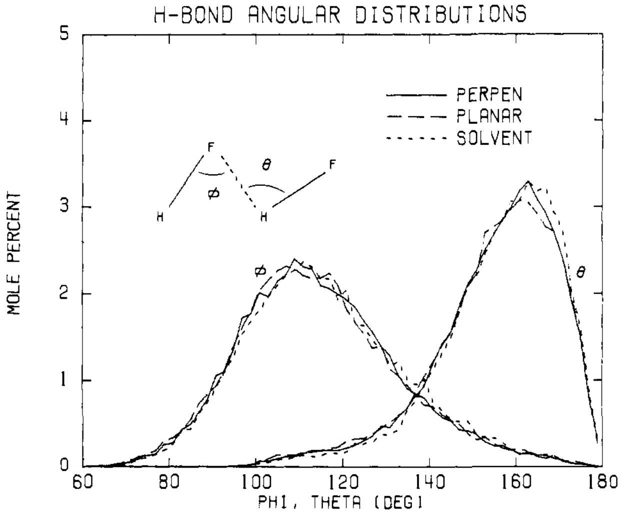

Figure 15. Distributions for the hydrogen-bonding angles θ (F···H–F) and ϕ(H–F···H). The units for the ordinate are mol % per deg.

Table VIII. Hydrogen Bond and Neighbor Analyses for Solvent Shells around the Planar Allyl Cation[a]

r(CF), Å	⟨HB⟩	$\langle N_{sx} \rangle$	$\langle e_{ss} \rangle$
0.0–3.5	0.95	4.02	-1.5
3.5–4.5	1.06	6.71	-2.3
4.5–5.5	1.70	6.89	-9.4
5.5–6.5	1.73	16.39	-10.2
6.5–7.5	1.86	20.14	-12.1
7.5–8.5	1.89	25.38	-12.1
8.5–9.5	1.89	44.05	-13.1
solution	1.82		-12.6
pure HF	1.82		-13.1

[a] ⟨HB⟩ is the average number of hydrogen bonds, $\langle N_{sx} \rangle$ is the average number of hydrogen fluoride monomers in the shell, and $\langle e_{ss} \rangle$ is the average total solvent–solvent bonding energy (kcal/mol) for monomers in the shell.

branched in the solutions to accommodate the solvent molecules nearest the ions. The distributions for the solvent–solvent hydrogen bond angles are shown in Figure 15. The results are again similar and the hydrogen bonds are found to be bent by an average of 20°.[20]

Further details on the solvent disruption were obtained by separately analyzing the hydrogen bonding for shells of the solvent centered around the central carbons (C1). The results are summarized in Table VIII and IX. The solvent molecules nearest the ions only participate in one solvent–solvent hydrogen bond; however, the bulk value of 1.8 hydrogen bonds per monomer is closely approached within ca. 6 Å of the ions. The average total solvent–solvent interaction energies for the HF monomers in each shell are reported as $\langle e_{ss} \rangle$. The results show significantly diminished solvent–solvent bonding within 5 Å of the ion. Moreover, the solvent disruption is largely confined to this region. In addition,

Table IX. Hydrogen Bond and Neighbor Analyses for Solvent Shells around the Perpendicular Allyl Cation[a]

r(CF), Å	⟨HB⟩	$\langle N_{sx} \rangle$	$\langle e_{ss} \rangle$
0.0-3.5	0.91	4.83	0.1
3.5-4.5	1.16	4.14	-2.5
4.5-5.5	1.65	9.24	-8.2
5.5-6.5	1.74	12.30	-10.0
6.5-7.5	1.90	21.96	-12.2
7.5-8.5	1.87	26.36	-12.2
8.5-9.5	1.88	43.59	-13.1
solution	1.82		-12.5
pure HF	1.82		-13.1

[a] ⟨HB⟩ is the average number of hydrogen bonds, $\langle N_{sx} \rangle$ is the average number of hydrogen fluoride monomers in the shell, and $\langle e_{ss} \rangle$ is the average total solvent–solvent bonding energy (kcal/mol) for monomers in the shell.

the disruption is somewhat greater for the perpendicular ion for which the nearest solvent molecules actually have slightly net repulsive solvent–solvent interactions. This has been observed previously for other ionic solutions and results from repulsive interactions between molecules in the first shell that are oriented for maximum bonding with the solute.[24,25] The average hydrogen bond strengths and hydrogen bond angles were also computed for each shell. No significant differences were found in comparison to the results for the pure solvent.

Conclusion

This work significantly extends a series of theoretical investigations of the solvation of carbonium ions and of solvent effects on their relative energies. Initially, a simple model for specific solvation of carbonium ions by HF was presented. Besides generating results that were consistent with experimental observations, the model proved to be a qualitative gauge for the solvation energy difference between isomeric carbonium ions.[7,15] For example, the difference in energy between the planar and perpendicular conformers of the allyl cation is calculated to be lowered by 6 kcal/mol when the ions are solvated by one HF and 13 kcal/mol for two HFs. This is consistent with recent analyses of NMR data for substituted allyl cations.[11] Furthermore, the above findings support the idea that given substantially different charge delocalization for isomeric cations, the relative energies should vary from the gas phase to solution.[4,7]

Of course, the concern remains that interactions with additional solvent molecules are needed before an adequate account of differential solvation of carbonium ions can be obtained. In this regard, the results of the statistical mechanical calculations presented in this work complete the analyses. The most striking outcome is that the qualitative trends provided by the quantum mechanical models for specific solvation are upheld. In particular, the more localized perpendicular allyl cation is found to be better solvated than the planar species. The formally charged carbon of the former is strongly coordinated with two HF monomers, while the planar ion is primarily solvated only through hydrogen bonds. Although the solvent disruption caused by the perpendicular conformer is greater than for the planar cation, the difference is not large enough to offset the weaker solvation of the resonant ion. Specifically, the difference in ion–solvent interaction energies (E_{sx}) is 25 kcal/mol, while there is only 4 kcal/mol more solvent disruption (ΔE_{ss}) caused by the perpendicular ion.

Besides demonstrating the importance of solvent effects on the relative energies of isomeric carbonium ions, the present work also provided detailed insights into the solvation of the allyl cation in liquid HF. The importance of hydrogen bonding in the solvation of carbonium ions is particularly notable. It was also found that the solvent disruption is primarily localized in the first shell of solvent molecules around the ions. Normal solvent–solvent hydrogen bonding is rapidly reestablished beyond this region. Furthermore, the present studies have well illustrated the utility of statistical mechanics methods for examining organic liquids and solutions at the molecular level. Though computationally demanding, such studies should become an increasingly valuable source of information on the solvation of molecules and intermediates and on the origin of solvent effects.

Acknowledgment. The authors are grateful to the National Science Foundation for support of this research and to Professor E. M. Arnett and Dr. J. Chandrasekhar for helpful discussions.

Registry No. Allyl cation, 1724-44-3; hydrogen fluoride, 7664-39-3.

Structure and Stability of Oxyallyl. An MCSCF Study

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Abstract: The structures of several low-lying states of oxyallyl ($\cdot CH_2COCH_2\cdot$) have been determined by ab initio MCSCF calculations. The ground state of oxyallyl is found to be $^3B_2$, but the first excited state ($^1A_1$) is located only 6 kcal/mol higher in energy. The $^1A_1$ state is best described as a diradical, with a strong C–O π bond and an electron largely localized at each of the peripheral carbon atoms. Two other singlet states, $^1B_2$ and $^1B_1$, lie 10-20 kcal/mol above $^1A_1$. The vibrational analysis of $^1A_1$ shows all real frequencies; therefore, oxyallyl appears to be a true intermediate of the ring opening of cyclopropanone.

Oxyallyl, $\cdot CH_2\text{–}CO\text{–}CH_2\cdot$, has been widely discussed as a possible transition state or an intermediate in several reactions,[2,3] for example, in the isomerization of cyclopropanone[4] and in the Favorskii rearrangement.[5,6] Semiempirical and ab initio studies[4,6] using the closed-shell SCF method suggest that the oxyallyl singlet is the transition state of disrotatory ring opening of cyclopropanone. However, as discussed below, the electronic state for this system

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