Hydrogen Bonding in Gas-Phase Anions. An Experimental Investigation of the Interaction between Chloride Ion and Brønsted Acids from Ion Cyclotron Resonance Chloride Exchange Equilibria

J. W. Larson[1a] and T. B. McMahon*[1b]

Contribution from the Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 6E2. Received August 25, 1983

Abstract: Ion cyclotron resonance chloride transfer equilibrium measurements have been used to establish an accurate scale of chloride ion binding energies for a variety of inorganic acids, carboxylic acids, alcohols, aldehydes, ketones, amines, and alkyl and aryl halides. Variation of chloride ion binding energy with gas-phase acidity reveals a far more pronounced effect of electrostatic interactions than existed for the fluoride ion. Results indicate in many cases multiple binding site interactions occur. Comparison of chloride affinities with bulk solvation abilities reveals similarities and differences between gas-phase and solution behavior that may be understood in terms of strength of interaction, molecular size, and molecular shape.

A significant number of studies have recently demonstrated the utility of thermochemical data for the binding of gas-phase ions to single neutral molecules as a convenient means of understanding bulk solvation phenomena and the transition from gas- to solution-phase ionic behavior.[2-6] Of particular interest have been studies of the binding of simple gas-phase anions, particularly halide ions, to Brønsted acids, since these are extremely common anions in solution. In the case of halide ions, the structural simplicity of the anion permits it to act as a very sensitive probe to intrinsic functional and structural variation in the Brønsted acid substrate. Such studies thus provide a convenient starting point for the construction of solvation models.

Recent work from this laboratory has resulted in the construction of an accurate scale of fluoride ion binding energetics[6] which has furthered the understanding of the nature of very strong hydrogen bonding interactions between anions and protic acids. This work has led to the characterization of functional group and structural factors affecting strong hydrogen bonds. The strength of the interaction of F⁻ with Brønsted acids is a direct result of its small size, high electronegativity, and relatively high basicity. Chloride ion, by contrast, is much larger, less electronegative, and significantly less basic. As a result, the strength of interaction of Cl⁻ with the same series of Brønsted acids is expected to be considerably reduced relative to that of F⁻.

Several experimental studies have previously been made of the binding of Cl⁻ to Brønsted acids in the gas phase.[7-12] Kebarle and co-workers,[7-9] using high pressure mass spectrometric (HPMS) clustering equilibria measurements, have determined the thermochemistry of binding of Cl⁻ to a variety of oxygen and carbon acids. Although ion cyclotron resonance (ICR) experiments are not suited to the general study of clustering phenomena,

bimolecular reaction sequences for the generation of gas-phase Cl⁻ adducts have been developed. Riveros[11,12] has shown that ClCO⁻ derived from dissociative electron attachment of Cl₂CO can transfer Cl⁻ to speices as weakly acidic as xenon and methyl chloride. Brauman[13] has generated the radical anion CF₃Cl⁻· from CF₃COCl and shown that this species can also act as an efficient Cl⁻-transfer reagent. These two methods, however, suffer from the disadvantages that the Cl⁻-donor anion is produced with extremely low cross section and that the neutral precursors themselves bind Cl⁻ relatively strongly so that they interfere seriously with Cl⁻-transfer reactions involving Brønsted acids of interest. Nevertheless, these two techniques have permitted a qualitative ordering of Cl⁻-binding energies for several compounds.

In order to circumvent these difficulties, we have recently developed bimolecular reaction sequences involving chloroformate esters that yield Cl⁻ donors in large abundance with little or no interference from self-attachment of Cl⁻.[14,15] In the present work, we wish to report a large body of bimolecular chloride exchange equilibria, eq 1, for several compounds already studied by HPMS

$$R_1H \cdots Cl^- + B_2H \rightleftharpoons R_2H \cdots Cl^- + R_1H \qquad (1)$$
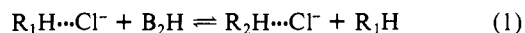
for comparison purposes and many other new compounds to allow elucidation of the molecular factors affecting binding energetics. One of the principle objectives in carrying out this work is the comparison of binding energies for Cl⁻ to compounds for which F⁻ attachment energies have been previously determined.[6] In so doing, we hope to obtain a better understanding of the ways in which these two different ions form hydrogen bonds. Theoretical studies[16-18] have indicated that F⁻'s form hydrogen bonds with considerable covalent character while chloride ions interact with most species in a far more electrostatic fashion. It was therefore of some interest to test this hypothesis with an extensive body of experimental data. In addition, because of the greater basicity of F⁻, proton abstraction competed with F⁻ attachment for many common solvent species of interest. The much lower basicity of Cl⁻ allows an extension of our studies of hydrogen-bonding and anion-binding energetics to many more Brønsted acids. As a result, the Cl⁻ ion provides a valuable model system for comparison of single molecule binding energetics and bulk solvation energetics.

(1) (a) On sabbatical leave from Marshall University, Huntington, WV. (b) After September 1, 1984, address correspondence to this author at the University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.
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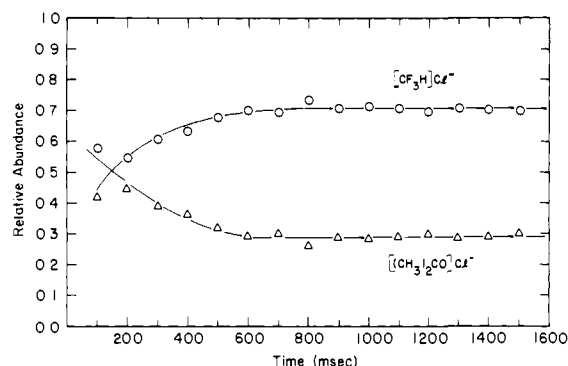(18) Yamabe, S.; Hirao, K. *Chem. Phys. Lett.* **1981**, *84*, 598.

Figure 1. Variation of relative negative ion abundances with reaction time for a 2.7:1:5:5 mixture of $ClCO_2CH_3$:CHF_3:$(CH_3)_2CO$ at a total pressure of 2.4×10^{-6} torr following a 5-ms, 70-eV electron beam pulse.

These advantages provide an opportunity for again investigating the effects of small changes in gas-phase acidity, polarity, and structure on the binding of anions and allow use of Cl^- as a sensitive probe for deducing intrinsic factors affecting solvation.

Experimental

All experiments were conducted at ambient temperature with an ICR spectrometer of basic Varian V-5900 design extensively modified to permit ion-trapping experiments.[19] Details of the design and operation of the trapped-ion ICR technique and conventional ICR single- and double-resonance experiments have been described in detail elsewhere.[20,21]

All chemicals are commerical samples of the highest purity obtainable. The materials were used without further purification with the exception of degassing prior to use of several freeze–pump–thaw cycles.

A typical chloride transfer equilibrium experiment involved introduction of methyl chloroformate ($ClCO_2CH_3$) into the ICR cell through a high-vacuum leak valve to a pressure of $\sim 6 \times 10^{-7}$ torr. Dissociative electron capture produced Cl^- which reacts subsequently via S_N2 displacement, eq 2.[14,15] A mixture of the two chloride-acceptor species, one

$$Cl^- + ClCO_2CH_3 \rightarrow ClCO_2^- + CH_3Cl \qquad (2)$$
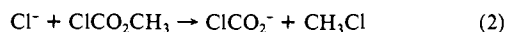
of which is a reference compound to known chloride affinity, is prepared with accurately known partial pressure with a Validyne AP-10 absolute pressure gauge on a Monel vacuum line. This mixture is then admitted to the ICR cell through a second leak valve to a pressure of 1×10^{-6} to 6×10^{-6} torr. The $ClCO_2^-$ ion acts as an excellent chloride donor, and Cl^- transfer to the Brønsted acids R_1H and R_2H readily occurs. The subsequent reversible chloride-transfer reaction, eq 1, led to steady-state abundances of R_1HCl^- and R_2HCl^- within about 300 ms. The relative ionic abundances were then monitored for at least twice the length of time needed to establish the steady state. Typical variation of relative ionic abundances with reaction time for chloride ion–Brønsted acid adducts is illustrated in Figure 1 for a mixture of $ClCO_2CH_3$, CF_3H, and $(CH_3)_2CO$.

While a persistent steady state was taken to be the initial indication of thermal equlibrium, confirmation was made by the following: (i) a calculated equilibrium constant that was invariant to changes in neutral pressure ratios and total pressure; (ii) multiple overlap experiments that led to closed thermochemical cycles; and (iii) double-resonance experiments at long reaction times to verify the occurrence of reaction in both forward and reverse directions.

Experimental details of methods for examining halide-exchange equilibria and alternative methods of generating chloride ion donors have been reported previously.[6,14,15] The chloride affinities of a series of reference compounds with properties making them convenient for use in ICR experiments have been summarized elsewhere.[14]

Results

Equilibrium constants for eq 1 were calculated from the experimentally observed steady state ionic abundances and manometrically determined neutral pressure ratios. Free energy changes for chloride transfer from the compounds of interest, R_1H, to reference compounds, R_2H, were calculated from eq 3. These

$$\Delta G^\circ_1 = -RT \ln K_{eq} \qquad (3)$$

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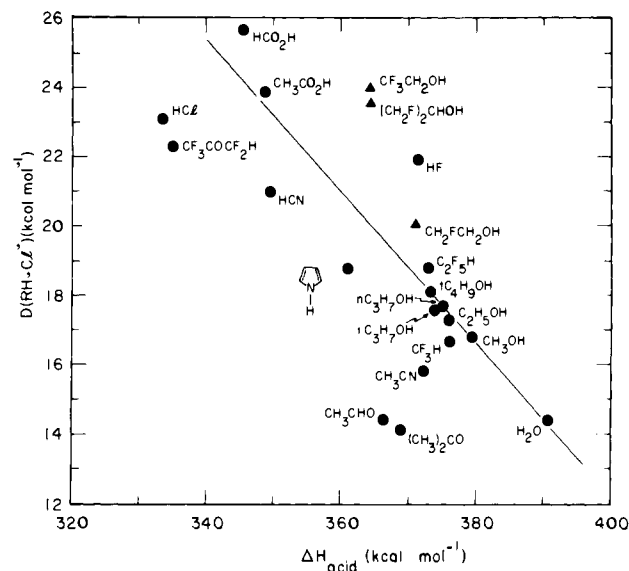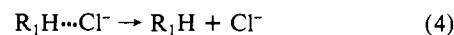

Figure 2. Variation of gas-phase chloride-binding energies with gas-phase acidities of Brønsted acids.

values are reported in Table I and have a maximum uncertainty of ± 0.2 kcal mol^{-1}. The free energy of dissociation of the chloride ion adduct, ΔG°_4, is then calculated from eq 5, where the values

$$R_1H\cdots Cl^- \rightarrow R_1H + Cl^- \qquad (4)$$

$$\Delta G^\circ_4(R_1H) = \Delta G^\circ_4(R_2H) - \Delta G^\circ_1 \qquad (5)$$

of $\Delta G^\circ_4(R_2H)$ have been previously accurately determined from ICR measurements of chloride-transfer equilibria[14] and high pressure mass spectrometric clustering equilibria.[7,9]

The entropies of dissociation of the chloride ion adducts, ΔS°_4, were calculated by using eq 6 developed from a statistical me-

$$\Delta S^\circ_4 = R\left(8.98 + 1.5 \ln \Delta H^\circ_4 - 2 \ln r + \ln \frac{\sigma_{RHCl^-}}{\sigma_{RH}} \right) \qquad (6)$$

chanical method outlined previously.[22] Here σ is the hydrogen-bond distance determined from ab initio calculations and estimates from analogous compounds,[16–18] and σ is the rotational symmetry number of the species involved. Values of ΔS°_4 and ΔH°_4 are also summarized in Table I. Also included, where available, are values determined by other methods for the same compounds. In general, values in the present work are in good agreement with those previously determined results.[7–12]

In several of the compounds investigated, more than one possible interaction site for Cl^- exists. In these cases, ΔS°_4 values are likely to be higher than those calculated from eq 6 because of the hindered internal rotation in $RHCl^-$. The values of ΔS°_4 and ΔH°_4 for these compounds may thus be considered to be lower limits.

Discussion

1. Comparison of F$^-$- and Cl$^-$-Binding Energies. The present results are in agreement with previous work which showed a rather small effect of gas-phase acidity on Cl^--binding energy.[9] A plot of chloride ion binding energy vs. gas-phase acidity, shown in Figure 2, has a slope of roughly 0.2 for a straight line drawn through the homologous series of aliphatic alcohols. This is in contrast to a slope of 0.5 obtained for F^- binding to alcohols reported previously.[6] It was previously concluded that a slope of 0.5 for such a plot provides experimental evidence for very strong hydrogen bonding,[5] that is hydrogen bonds with appreciable covalent character. The present data thus provide further evidence that Cl^- binding to Brønsted acids has a significantly greater

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Table I. Thermochemical Data for Chloride Ion Adducts of Selected Brønsted Acids

R_1H	R_2H^a	$\Delta G^\circ_1{}^b$	$\Delta G^\circ_4{}^b$	$\Delta H^\circ{}^b$	$\Delta S^\circ{}^c$
Inorganic Acids					
HCl^d			16.0	23.1	23.5
HF	SO_2	+0.43	15.1	21.8	22.5
HCN^d			13.9	21.0	23.7
H_2O^d			8.4	14.4	20.1
NH_3	MeF	−0.91	4.5	10.5	19.9
Alkyl and Aryl Halides					
CH_3F	CH_3Cl	−0.67	5.4	11.5	20.3
CH_3CN	CF_3H	−0.41	9.4 $(9.2)^e$	15.8	21.4
CH_3Cl			6.1	12.2	20.5
CH_3Cl_2	CF_3H	−0.69	9.2 $(8.9)^f$	15.8	22.1
$CHCl_3$	CF_3H	1.36	11.2 $(10.3,^g\ 11.8^f)$	18.1	23.2
$CHFCl_2$	CF_3H	0.89	10.7	17.6	23.1
CHF_2Cl	$CHCl_3$	−1.0	10.3	17.2	23.0
	CHF_3	0.59			
CHF_3			9.8	16.7	22.9
CH_3CF_2H	CF_3H	−1.66	8.1	14.9	22.7
	$t\text{-}C_4H_9F$	0.90			
CH_2FCF_2H	C_2F_5H	−0.24	11.4	~18.9	~25.0
	$t\text{-}C_4H_9OH$	0.22			
CF_3CF_2H			11.8	18.8	23.3
$t\text{-}C_4H_9F$			7.1	13.3	20.8
$t\text{-}C_4H_9Cl$	$t\text{-}C_4H_9F$	0.89	8.0	14.3	21.2
C_6H_6			4.8	9.9	17.1
C_6H_5Cl			6.9	13.6	22.4
$o\text{-}C_6H_4F_2$	CH_3OCOCl	−0.03	7.8	14.3	21.6
$m\text{-}C_6H_4F_2$	$MeOCOCl$	−0.05	7.8 $(7.7)^h$	14.6	22.6
$p\text{-}C_6H_4F_2$	$MeOCOCl$	−0.51	7.3	13.8	21.6
Carboxylic Acid					
HCO_2H			18.4	25.6	24.1
$MeCO_2H$			16.7	23.9	24.0
Aldehydes					
MeCHO	$t\text{-}BuF$	0.77	7.9	14.4	21.7
Me_3CCHO	CF_3H	−1.36	8.4	15.0	21.9
Ketones					
Me_2CO			8.2	14.1	19.6
(Me)(Et)CO	PF_3	0.66	8.5	14.8	21.0
	Me_2CO	0.28			
Et_2CO	Me_2CO	0.00	8.2	14.1	19.6
Alcohols					
MeOH			9.9	16.8	22.9
EtOH	MeOH	0.61	10.4	17.3	23.1
	$t\text{-}BuOH$	−0.74			
$n\text{-}PrOH$	MeOH	0.90	10.8	17.7	23.2
	$t\text{-}BuOH$	−0.40			
$i\text{-}PrOH$	MeOH	0.81	10.7	17.6	23.2
	$t\text{-}BuOH$	−0.46			
$n\text{-}BuOH$	MeOH	0.75	10.7	17.6	23.2
$t\text{-}BuOH$			11.1	18.1	23.4
FCH_2CH_2OH			13.0	~20.5	~25.0
$ClCH_2CH_2OH$	FCH_2CH_2OH	1.02	14.0	~21.5	~25.0
	SO_2	−0.74			
$(CH_2F)_2CHOH$	SO_2	1.19	16.1	~23.6	~25.0
	$MeCO_2H$	−0.40			
CF_2CH_2OH	SO_2	1.80	16.5	~24.0	~25.0
	$MeCO_2H$	−0.21			
$(CF_3)_2(CH_3)COH$	HCO_2H	≥1.20	≥19.0	≥26.5	~25.0
$(CF_3)_2CHOH$	$(CF_3)_2CH_3COH$	>0.0	>19.0	>26.5	~25.0
Amines					
	$t\text{-}BuOH$	1.65	11.8	18.8	23.4
	FCH_2CH_2OH	−0.26	$(14.0)^d$		
$CF_3CH_2NH_2$	CF_3H	0.96	10.8	~18.0	~24.0

[a] Reference species with previously determined accurate chloride ion binding thermochemistry. [b] kcal mol⁻¹. [c] cal/deg K·mol, 1 atm of pressure. [d] These species are themselves reference acids (R_2H). [e] Reference 10. [f] Reference 12. [g] Reference 2. [h] Reference 7.

electrostatic character than F⁻ binding.

Hydrogen bonds to Cl⁻ appear also to be much less sensitive to the heteroatom associated with the acidic proton than are F⁻–hydrogen bonds. For example, ethanol and fluoroform, with nearly equal gas-phase acidities, have chloride affinities which differ by only 0.6 kcal mol⁻¹ in favor of the alcohol while, in contrast, fluoride binding to ethanol is 4.4 kcal mol⁻¹ more favorable than that to CHF_3. In both cases, however, ethanol with
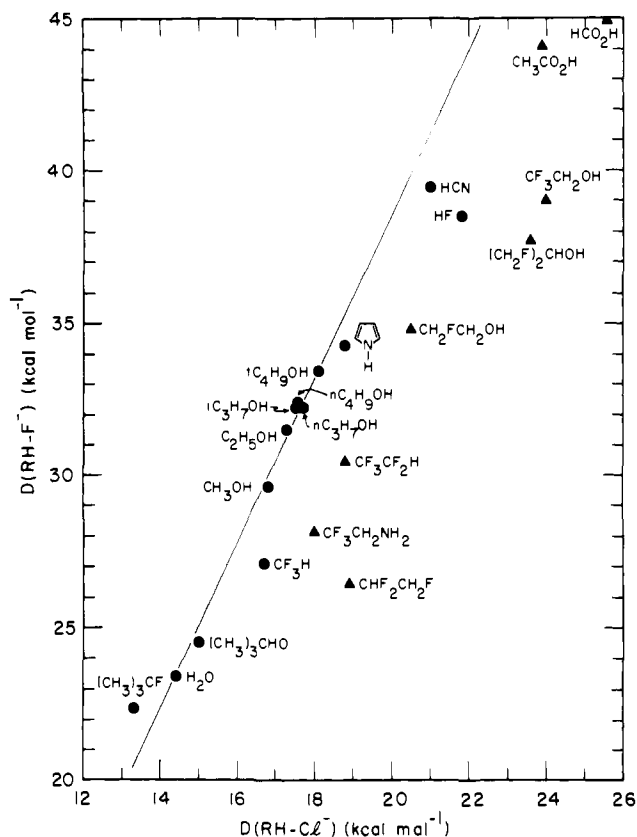
45 ─ HCO₂H ▲
CH₃CO₂H ▲

40 ─ ● HCN   CF₃CH₂OH
HF ●   ▲
ICH₂F)₂CHOH ▲

D(RH-F⁻) (kcal mol⁻¹)

35 ─   ▲CH₂FCH₂OH
IC₄H₉OH ●
IC₃H₇OH ● nC₄H₉OH
C₂H₅OH ●   nC₃H₇OH

30 ─   ▲CF₃CF₂H
CH₃OH ●

         ▲CF₃CH₂NH₂
● CF₃H   ▲CHF₂CH₂F

25 ─   ● ICH₃)₃CHO
ICH₃)₃CF ● H₂O
●

20 ─
12   14   16   18   20   22   24   26

D(RH-Cℓ⁻) (kcal mol⁻¹)

Figure 3. Variation of gas-phase chloride-binding energies with fluoride-binding energies of Brønsted acids.

Table II. Comparison of Electrostatic Interaction Energies and Experimental Dissociation Energies of RH–Cl

species	E_{el},[a] ΔH°_4,[a]	species	E_{el},[a] ΔH°_4,[a]
Cl–HF	20.5, 21.8	Cl⁻–H₃CF	10.0, 11.5
Cl⁻–HCN	19.5, 21.1	Cl⁻–H₃CCN	11.8, 15.8
Cl⁻–H₂O	14.1, 14.4	Cl⁻–acetone	13.5, 14.2
Cl⁻–H₃N	7.2, 10.6	Cl⁻–C₆H₆	8.7, 9.9
Cl⁻–H₃CH	3.2, –	Cl⁻, o-C₆H₄F₂	13.0, 14.3
Cl⁻–HCl	13.5, 23.3	Cl⁻, m-C₆H₄F₂	14.8, 14.6
Cl⁻–HCCl₃	21.5, 18.1	Cl⁻, p-C₆H₄F₂	12.0, 13.8
Cl⁻–H₂CCl₂	16.6, 15.8	Cl⁻–HO₂CH	14.1, 25.6
Cl⁻–H₃CCl	9.9, 12.2	Cl⁻–HO₂CMe	14.2, 23.9

[a] All values in kcal mol⁻¹.

the more electronegative heteroatom forms the stronger hydrogen bond.

A general comparison of F⁻- and Cl⁻-binding energetics is shown in Figure 3 for a plot of RH···F⁻ vs. RH···Cl⁻ hydrogen-bond strengths. In spite of the difference in the nature of the hydrogen bond for the two anions, a generally linear relation is observed although large deviations are observed. This qualitatively linear relationship between the single molecule solvation energies of the two anions is a necessary requirement if a single anion solvation parameter characteristic of the solvent, such as that proposed by Swain,[23] is to be successful. It is noteworthy that in our parallel studies of anion-binding energetics to Lewis acids[24] no such linear correlation exists, implying that a single solvent parameter for aprotic solvents will very likely be a poor model.

Several of the compounds included in the present study (denoted by triangles in Figure 3) are capable of multiple interactions with anions. In each of these cases the chloride ion adducts are more stable than would be predicted from the fluoride ion binding data. These data thus provide further evidence of the electrostatic nature of Cl⁻ binding and of the ability of Cl⁻ to favor cooperative binding because of the less severe geometric constraints associated with binding the bulkier Cl⁻ ion. By contrast, the covalent nature of F⁻ binding leading to stronger and therefore shorter hydrogen bonds places far more severe geometric constraints on the adduct conformation making multiple binding less favorable. In this report, these "multidentate" compounds might be considered to be "softer" acids.[25] In this case, however, they are softer due to greater polarizability caused by conformational change rather than due to more polarizable atoms. As a result, these "softer" acids bind more favorably to the soft base Cl⁻ than the harder F⁻.

2. Electrostatic Interactions. In order to test the conjecture that hydrogen bonding of chloride ion is appreciably electrostatic, it was of interest to examine the extent to which a simple elec-

trostatic model can quantitatively account for the experimentally determined chloride affinities. The electrostatic energy E_{el} has been calculated from the sum of ion–permanent dipole interactions, $E_{\mu z}$, ion–induced dipole interactions, $E_{\alpha z}$, and an electronic repulsion term, E_{rp}. A point charge model[2,26] has been used to represent the neutral molecule with the point charges, q_i, calculated from appropriate bond moments and $E_{\mu z}$ then calculated from eq 7. Atomic polarizabilities were used to calculate the ion–induced

$$E_{\mu z} = e\sum_i \frac{q_i}{r_i} \quad (7)$$

dipole term from eq 8. Because of the difficulty is esimating the

$$E_{\alpha z} = -\frac{e^2}{2}\sum_i \frac{\alpha_i}{r_i^4} \quad (8)$$

coefficient of the A/r^{12} repulsive term, equilibrium H–Cl⁻ distances of 2.13, 2.68, 3.22 Å were estimated for Cl⁻ binding to one, two, and three hydrogens, respectively. Differentiation of the energy equation with respect to r_i led to the result that E_{rp} must be equal to $-E_{\mu z}/6 - E_{\alpha z}/3$ at the equilibrium distance. Electrostatic interaction energies thus calculated are given in Table II together with the experimental ΔH°_4 values. Good agreement between E_{el} and ΔH°_4 values is obtained for the first period hydrides and for carbon acids. The strong acids HCl, HCO₂H, and CH₃CO₂H give much more stable chloride adducts than predicted by the electrostatic calculation, indicating that in these species considerable delocalization of negative charge into the Brønsted acid RH is occurring resulting in more stable bonding. This is exactly the result that would have been expected on an intuitive basis for strong acids. As the gas-phase acidity of RH increases, a larger extent of proton transfer will occur within the chloride adduct. Although none were investigated in the present work, adducts of acids with gas-phase acidity sufficiently greater than HCl would be more correctly regarded as R⁻ coordinated to HCl.

3. Comparison of Single Molecule Solvation Energies and Bulk Solvent Solvation. Recently, Swain et al.[23] have carried out a statistical analysis of solvent effects on rates, equilibria, and spectral shifts and found that virtually all solvent effects can be accounted for by two solvent properties, A, the "acity" of the solvent, and B, the "basity" of the solvent. A is a measure of the ability to solvate anions, and B is a measure of the ability to solvate cations. It is of some interest then to compare the solution phase A values for common solvents to the values of halide ion single molecule solvation energies. Such a comparison is shown in Figure 4 for a plot of acity vs. Cl⁻-binding energy. From this figure it is immediately apparent that for nonpolar and dipolar aprotic solvents, there is an apparently good qualitative coorelation between solvent acity and chloride-binding energy. The aliphatic alcohols and water, however, show a marked reversal in correlation of acity and chloride ion binding energy. Water, which in the condensed phase is one of the most effective solvating agents, is in the gas phase a quite unremarkable anion-binding agent. Proceeding through the series of aliphatic alcohols as gas-phase acidity and chloride ion binding energy increase, the solvent acity function actually drops off markedly. This difference in bulk

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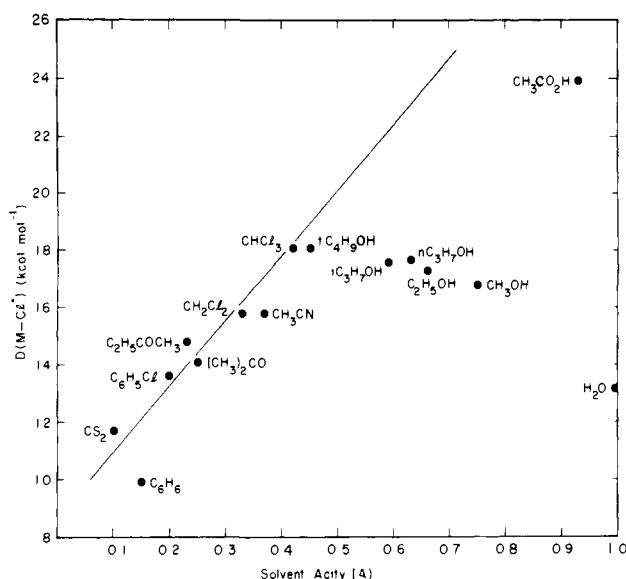(26) Muirhead, J. S.; Laidler, K. J. *Trans. Faraday Soc.* **1967**, *63*, 944.

Figure 4. Variation of gas-phase chloride-binding energies with the Swain acity parameter, *A*.

solution and gas-phase solvatory abilities appears to be quite clearly a function of molecular size. The large size and structural complexity of the higher alcohols makes it much more difficult to have more than a few solvent molecules interacting with a single anion, whereas the small size of the water molecule makes multiple interactions with a single anion much more feasible. In cases such as this, the single molecule solvation energies do not give a realistic depiction of bulk solvating ability.

Conclusion

We have demonstrated that a qantitative scale of chloride ion binding energies for a wide variety of Brønsted acids has been established. The variation of chloride-binding energies with gas-phase acidities has shown that chloride binds protic substrates with far more electrostatic character than does the fluoride ion. Also, unlike the fluoride ion, a consistent variation of chloride affinity with gas-phase acidity does not hold for complex alcohols because of multiple binding site interactions which are far more favorable for Cl$^-$ than for F$^-$. A comparison of chloride affinities with solution phase anion solvation ability ("acity") reveals a good correlation for nonpolar and dipolar aprotic solvents but an inverse correlation for protic, hydroxylic solvents. These, and related data from our laboratory, are being used to provide a basis for understanding molecular factors effecting the solvation process.

Generation and Identification of Four Stable Isomeric [C$_3$H$_3$]$^+$ Ions by Direct Dissociative Ionization or by Charge Reversal of Anions

Peter C. Burgers, John L. Holmes,* Alexander A. Mommers, and Jan E. Szulejko

Contribution from the Chemistry Department, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4. Received July 6, 1983

Abstract: Examination of collisional activation mass spectra showed that pure [cyclopropenium]$^+$ was generated by only metastably fragmenting precursor ions, [C$_4$H$_6$]$^+$·, [C$_3$H$_3$Br]$^+$·, and [C$_3$H$_3$Cl]$^+$·. Pure [CH$_2$=C=CH$^+$] could be produced from the dissociative ionization of [CH≡CCH$_2$I] in the ion source and among metastably fragmenting ions. The ions [CH$_2$=CH—C:$^+$] and [CH$_3$C≡C$^+$] were generated by collisionally induced charge inversion of the corresponding anions. The latter were produced by dissociative electron capture and by reaction of OH$^-$ with cyclopropene and CH$_3$C≡CD, respectively. Although [CH$_2$=CH—C:$^+$] exists in a potential well, [CH$_3$C≡C$^+$] ions produced by the above method lie close to their dissociation limit. [CH$_2$=C=CH$^+$] and [CH$_2$=CH—C:$^+$] ions generated by charge reversal rearrange to similar mixtures of [cyclopropenium]$^+$ and [CH$_2$=C=CH$^+$] within a time of ca. 8 μs. The fragmentations [C$_3$H$_5$]$^+$ → [C$_3$H$_3$]$^+$ + H$_2$ and [C$_5$H$_5$]$^+$ → [C$_3$H$_3$]$^+$ + C$_2$H$_2$ produce composite metastable peaks. The high and low kinetic energy release components therein were shown to result from the generation of [cyclopropenium]$^+$ and [CH$_2$=C=CH$^+$], respectively.

Two isomeric [C$_3$H$_3$]$^+$ ions have been experimentaly observed, the cyclopropenium and propargyl cations. The heat of formation, ΔH_f°, of the former has been well established by a variety of measurements[1] as 255 ± 1 kcal mol^{-1} and that of the latter as 281 ± 2 kcal mol^{-1}.[1,2] These experimental values have adequately

been reproduced by ab initio calculations[3] where the difference in their ΔH_f° values was found to be 31 kcal mol^{-1}. Previous calculations[4] indicated that two other structures were stable below the dissociation of lowest energy requirement to [C$_3$H]$^+$ + H$_2$

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