Thermodynamic Study of Hydrogen Bonding to Chloride Ions

S. Y. Lam, C. Louis, and R. L. Benoit*

Contribution from the Département de Chimie, Université de Montréal, Montreal, Quebec, H3C 3V1, Canada. *Received May 15, 1975*

Abstract: The equilibrium constants, K, and enthalpy changes, $\Delta H_f(\text{l})$, for the 1:1 association reaction between chloride ion and a variety of proton donors, HR, have been determined at 30°C in sulfolane. Thermodynamic data for the association of Cl^- with substituted acetic acids as HR were also obtained at 25°C in acetonitrile, dimethylformamide, and dimethyl sulfoxide. The experimental methods used involved solubility and vapor-pressure measurements, proton NMR, and calorimetry. The order of increasing donor strength of HR based on $\Delta H_f(\text{l})$ (kcal mol^{-1}) in sulfolane is $HCCl_3$ (−2.1) < HOH (−2.6) < $HCH_3O \sim HCH_3CO_2$ (−3.2) < HC_6H_5O (−3.6) < $HCO_2H \sim HCF_3CO_2$ (−4.0) ≪ HCl (− 8.1). The enthalpy changes, $\Delta H_s(\text{HR})$, for the process $HR(g) \rightarrow HR(l)$ were also determined. Comparisons of our $\Delta H_f(\text{l})$ and $\Delta H_s(\text{HR})$ data with reported $\Delta H_f(\text{g})$ values for the gas-phase reaction $Cl^-(g) + HR(g) \rightarrow ClHR^-(g)$ permit a complete analysis of the solvent effect on this hydrogen-bonding reaction. Both the change in the order of donor strength and the widening of donor strength range on passing from sulfolane to the gas phase are accounted for by differences in the solvation enthalpies ΔH_s of both HR(g) and $ClHR^-(g)$. The calculated enthalpy change for $Cl^-(l) + HR(g) \rightarrow ClHR^-(l)$ appears to vary only slightly with the three solvents studied. This agrees with findings for other anion-molecule reactions with dipolar aprotic solvents.

Hydrogen-bonding equilibria between anions X^- and proton donors HR have been studied both in weakly polar[1,2a] and dipolar aprotic[2b-6] solvents. Correlations have, not surprisingly, been sought, for a given ion X^-, between some proton donor properties of HR and the equilibrium constant K of the association reaction

$$X^-(l) + HR(l) \rightleftarrows XHR^-(l) \quad (1)$$

For a series of related donors, HR, K increases with the acid strength of HR.[5] Thus, linear correlations have been established between log K and the σ Hammett parameters of the substituents in a series of carboxylic acids[4,6] and phenols.[3] However, somewhat unexpectedly, log K shows a low sensitivity to the σ parameters, particularly in the more basic solvents.[5,6] It would appear that the effectiveness of HR as a proton donor to bind X^- is low because there is a competing interaction of HR with solvent molecules.

Arnett and co-workers[7] have convincingly shown that a full understanding of the many factors influencing the protonation of bases in solution, i.e., a reaction related to reaction 1, could be gained from a comparison of the thermodynamics of such reaction in gas and condensed phases. The gas-phase enthalpy data of Kebarle[8] for the reaction

$$Cl^-(g) + HR(g) \rightarrow ClHR^-(g) \quad (2)$$

using a series of proton donors, HR, provide us with an opportunity to analyze the solvent effect on such a hydrogen bonding reaction, once we establish the corresponding thermodynamic data in a particular solvent.

The present work was therefore undertaken to obtain thermodynamic data for reaction 1 between Cl^- and the series of proton donors HR: chloroform, methanol, acetic acid, phenol, and formic and trifluoroacetic acids. Sulfolane was used as solvent so that we could also add to the series our previous results obtained with HR = HOH and HCl.[9,10] Additional determinations were made in three other dipolar aprotic (dpa) solvents, acetonitrile (AN), dimethylformamide (DMF), and dimethyl sulfoxide (Me_2SO), with HR = XCO_2H. The experimental methods used to obtain the association constant, K, for reaction 1 involved solubility, proton NMR, and water vapor pressure measurements. Calorimetric determinations were carried out to obtain the corresponding enthalpy changes, $\Delta H_f(\text{l})$, as well as the solution enthalpies, $\Delta H_s(\text{HR})$, of the gaseous proton donors.

Experimental Section

Materials. Sulfolane from Shell was treated according to a method given earlier.[11] Certified spectroanalytical Me_2SO from Fisher and reagent Anachemia DMF were treated with 4A molecular sieves heated at 200°C, decanted, and distilled under vacuum. Middle portions were collected. Eastman reagent AN was used as received. The water content of these solvents was less than 0.005 M as determined by Karl Fischer titration. Anachemia reagent sodium and potassium chlorides had a purity of 99.9%. Tetraethylammonium chloride from Eastman, recrystallized from a mixture of 5% ethanol and 95% ether and dried in a vacuum oven at 40° for 24 h, had a purity of 99.9%. Practical formic acid from Eastman was recrystallized four times by freezing. Glacial acetic acid from CIL, Fisher chloroacetic and trifluoroacetic acids, and Baker dichloroacetic acid were used as received. All these acids had a minimum purity of 99.5%. Spectroanalyzed methanol from Fisher was dried with 4A molecular sieves and distilled. Baker analyzed reagent chloroform was refluxed in presence of metallic sodium overnight and distilled. Crystals of Baker reagent phenol after evacuation to remove water, had a 0.02% water content. Baker reagent toluene and Aldrich 1,3,5-trichlorobenzene were used as received.

Solubility Measurements. Solubility measurements at 25°C were made on KCl in Me_2SO, and NaCl in DMF solutions both containing variable concentrations of acetic (<0.8 M), chloroacetic (<0.5 M), dichloroacetic (<0.2 M), and trifluoroacetic acids (<0.2 M). Total solubilities of these alkali chlorides were determined by potentiometric titration with standard silver nitrate.

Proton Magnetic Resonance. NMR measurements were carried out with a 60-MHz JEOL spectrometer at 24°C. Sulfolane solutions of 0.1 M acetic, formic, and trifluoroacetic acids with 0-0.5 M Et_4NCl in sulfolane were prepared by mixing sulfolane (0.001 M H_2O), 0.5 M Et_4NCl-sulfolane (0.002 M H_2O), and the pure acids. Sulfolane and its chloride solution were refluxed in high vacuum at 70°C prior to the experiments in order to eliminate water. For preparation of 0.1 M phenol solutions, a 1.1 M stock solution (0.002 M H_2O) was used. Water contents of these sulfolane solutions were: ~0.003 M for acetic and trifluoroacetic acids and phenol solutions; ~0.005 M for formic acid solutions. Solutions of 0.1 M toluene in AN and 1,3,5-trichlorobenzene in sulfolane were prepared likewise. A series of 0.22 M acetic acid solutions with 0-0.5 M Et_4NCl in DMF was also studied. Resonance signals of acidic protons measured with reference to those of sulfolane β-methylene protons or AN and DMF methyl protons are reported in parts per million relative to internal tetramethylsilane.

Vapor Pressure Measurements. Vapor pressures were measured with a Texas Instruments quartz spiral gauge. The cell containing the magnetically agitated solution was kept in a water bath at 30°C. The tubing, connecting the cell with the gauge kept at 58°C, was heated at 40°C. Degassing of the solution was performed by

Table I. Association Constants K (l. mol^{-1}) of 1:1 Complex between HR and Cl^- in dpa Solvents at 25°C

	dpa solvents			
HR	Me_2SO (solub)	DMF (solub)	Sulfolane^a	AN
$HCCl_3$			1.8 (K_2 ~ 0.5) (VP)	1.2^f (NMR)
HMeO			6.5 (K_2 ~ 3) (VP)	
HOH	0.6^d		8.2^d (K_2 ~ 3) (VP)	8^d (NMR)
HPhO			160^b (NMR)	
HCH_3CO_2	0.6	20,^{c} 11	120^b(NMR)	300^c (solub)
HCO_2H			250^b(NMR)	
HCH_2ClCO_2	2.1	25		500^c (solub)
$HCHCl_2CO_2$	2.1	27		2500^c (solub)
HCF_3CO_2	3.0	83	~1000 (NMR)	
HCl			250^e (NMR)	

^{a} 30°C. ^{b} Converted into values at 30°C using enthalpies of complex formation. ^{c} Reference 14. ^{d} Reference 9. ^{e} Reference 13. ^{f} Reference 15.

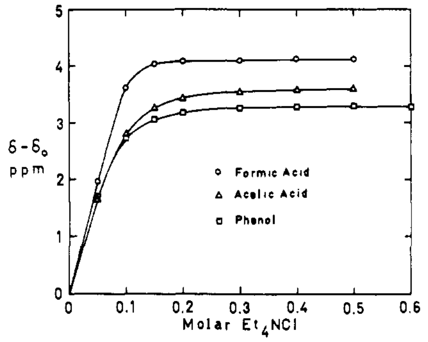


Figure 1. Chemical shifts of 0.1 M proton donors in sulfolane as a function of Et_4NCl concentration.

repeating freezing and evacuation. Sulfolane solutions containing 0.5 M chloride and variable concentrations of methanol and chloroform were prepared by weighing. The exact methanol concentration in solution was determined after measurement of the vapor pressure by comparison of the ir absorbance at ~2.04 μ with a preconstructed calibration curve. The chloroform concentration was found by weighing the cell before and after the vapor pressure determination, the loss of weight being that of chloroform.

Calorimetry. The calorimetric procedure and apparatus have been given before.[10] The heats of mixing known weights of the hydrogen-bond donors, HR, with 27 ml of 0.5 M Et_4NCl-sulfolane at 30°C (0.2 M Et_4NCl-AN at 25°C; 0.25 M Et_4NCl-DMF at 25°C) were determined for HR concentrations below 0.15 M. From three to seven determinations were made for each donor. The heats of mixing of HR with the pure solvents were obtained in the same manner as those for HR concentrations below 0.5 M.

Results

Solubility. The increase in total solubilities of KCl in Me_2SO and NaCl in DMF in the presence of carboxylic acids was interpreted in terms of complex formation between acids and chloride ions.[9] Corrections were made for ion-pair formation between Cl^- and K^+ or Na^+. It was assumed that only the 1:1 complex between donors and Cl^- was formed at low donor concentration. The equilibrium constants for reaction 1 were calculated from the relevant mass action and mass balance equations. For the calculation of K for $ClHCF_3CO_2^-$, the dissociation of HCF_3CO_2 and the formation of HCl were taken into account.[12] Results are given in Table I.

Proton Magnetic Resonance. The chemical shift of a hydroxyl proton of 0.2 M acid in DMF was measured for concentrations of chloride from 0 to 0.5 M. It was found that the chemical shift of the acidic proton varied from 12.00 to 12.63 ppm with added chloride from 0 to 0.5 M. The small variation did not allow a fair evaluation of the 1:1 complex constant, but only that of the complex shift δ_1, ~12.6 ppm.[12]

In sulfolane, the hydroxyl proton of 0.10 M formic, acetic, and trifluoroacetic acids gave defined but somewhat broad peaks with a mid-width of 0.1-0.2 ppm, while the hydroxyl proton of phenol and the methyl protons of toluene in AN solutions were sharp. The chemical shift of the methyl protons of toluene, and the ring protons of 1,3,5-trichlorobenzene changed by less than 0.04 ppm on addition of chloride. Other pertinent results expressed as the differences of chemical shifts of the hydroxyl proton in chloride solutions and those in pure solvents, δ-δ_0, are given in Figure 1 as a function of Et_4NCl concentration. The treatment for obtaining values of the 1:1 complex formation constant K and complex shift δ_1 is essentially as described earlier.[9] Our results for sulfolane together with values for AN are given in Table I. The highest values of K are somewhat approximate since the curvature of the plots of δ-δ_0 vs. chloride concentration on which the calculation of K depends diminishes when K increases.[13] It was noted that the chemical shift of the formyl proton of HCO_2H changed from 5.98 to an asymptotic 6.24 ppm when Cl^- concentration was increased from 0 to the vicinity of 0.1 M, while the chemical shift of the OH proton of HCO_2H also began to level off at ~0.15 M Cl^-. The change of the chemical shift of the formyl proton is likely to be due to the transmission of the -OH—Cl^- bonding effect through the molecular skeleton rather than to $\geqslant$CH—Cl^- bonding.

Vapor Pressure. The vapor pressure method proved convenient to study complex formation of Cl^- with chloroform and methanol because of their high vapor pressure over sulfolane solutions. The partial pressures of $HCCl_3$ and HCH_3O were obtained by subtracting the very small vapor pressure of sulfolane, 0.02 mm from the measured total pressure at 30°C. These vapor pressures are given in Figure 2 for 0.5 M tetraethylammonium chloride solutions as a function of concentrations of $HCCl_3$ and HCH_3O. These data were treated by the method previously used to study complex formation between Cl^- and HOH.[9] The assumptions implied in this treatment have also been discussed. Values of association constants K, and K_2 for 1:2 complexes in a few cases, are given in Table I.

Calorimetry. The heats of mixing of the proton donors with sulfolane, AN, and DMF are given in Table II. These heats are averages of three values or more for concentrations between 0.02 and 0.5 M. There was no concentration effect but for acetic acid in acetonitrile, above 0.2 M.[12] Except in the latter case, carboxylic acids are present as monomers in these solutions. The heats of mixing of the proton donors were determined at usually three averaged low concentrations C_{av}, in presence of 0.50 M Cl^- in sulfolane and 0.20 M Cl^- in AN. Data are reported in Table II. The heat changes were taken as the sum of two contributions: the en-

Table II. Heats of Mixing (kcal mol^{-1}) of Proton Donors

			(0.5 M Cl^-)			(0.2 M Cl^-)	
HR	Sulfolane	Sulfolane	C_{av}, M	AN	AN	C_{av}, M	DMF
$H_3CC_6H_5$	0.26 ± 0.01	0.31	0.068				
HCH_3O	1.40 ± 0.01	−0.94 ± 0.01	0.068				
$HCCl_3$	−0.97 ± 0.01	−1.94 ± 0.01	0.058				
HC_6H_5O	1.52 ± 0.01	−2.11 ± 0.02	0.050				
HCH_3CO_2	0.90 ± 0.02	−2.27 ± 0.02	0.063	1.02 ± 0.01	−1.00 ± 0.05	0.082	−1.97 ± 0.02
HCO_2H	0.10 ± 0.01	−3.87 ± 0.03	0.058				
HCH_2ClCO_2				3.56 ± 0.04	1.41 ± 0.02	0.065	−0.26 ± 0.01
$HCHCl_2CO_2$				−1.50 ± 0.02	−3.90 ± 0.02	0.048	−6.40 ± 0.02
HCF_3CO_2	−1.46 ± 0.01	−5.52 ± 0.02	0.080	−1.77 ± 0.02	−4.54 ± 0.08	0.062	−7.01 ± 0.02

Table III. Enthalpies (kcal mol^{-1}) of Complex Formation, $\Delta H_f(l)$ and $\Delta H_f(g)$, of $ClHR^-$ and Solvation Enthalpies ΔH_s of HR and $ClHR^-$

	Sulfolane[a]			AN[b]		Gas[b, c]
HR	$\Delta H_f(l)$	$\Delta H_s(HR)$	$\Delta H_s(ClHR^-)$[j]	$\Delta H_f(l)$	$\Delta H_s(HR)$	$\Delta H_f(g)$
$HCCl_3$	−2.1	−8.9[g]	+4.3	−2.0[d]	−8.3[g]	−15.2
HOH	−2.6	−8.9	+1.6	−2.1	−8.5	−13.1
HCH_3O	−3.2	−7.5[e]	+3.4			−14.1
HC_6H_5O	−3.7	−14.6[g]	+1.1			−19.4
HCH_3CO_2	−3.2	−11.4[f]	+7.0	−2.1	−11.2[f]	−21.6
HCO_2H	−4.0	−11.0[e]	+22.2			−37.2
HCH_2ClCO_2				−2.2	−15.0[f]	
$HCHCl_2CO_2$				−2.4	−15.7[f]	
HCF_3CO_2	−4.0	−13.4[f]		−2.8	−13.7[f]	
HCl	−8.1[i]	−5.8[h]	+9.8		−5.7[h]	−23.7

[a] 30°C. [b] 25°C. [c] Reference 8. [d] Calculated from calorimetric measurements and K from ref. 15. [e] Reference 17. [f] Reference 12. [g] Reference 18. [h] Reference 16. [i] Reference 10. [j] Expressed with respect to $\Delta H_s(Cl^-) = 0$.

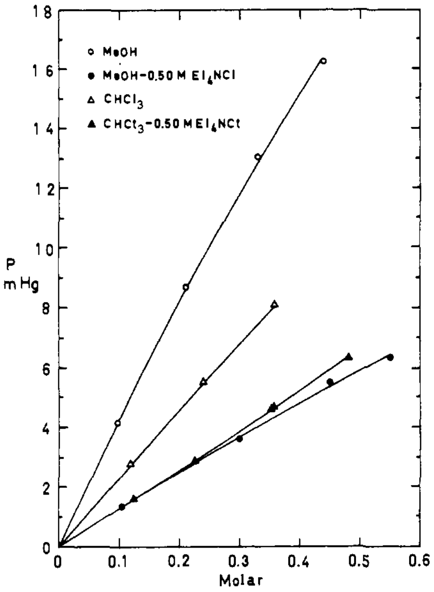


Figure 2. Vapor pressures of methanol and chloroform as a function of their concentration in sulfolane and 0.5 M Et_4NCl-sulfolane.

thalpy of mixing of the proton donor with the pure solvent and the enthalpy of association of the 1:1 complex. The K values listed in Table I were used to calculate the concentrations of the unbound proton donor and 1:1 complex. For K values larger than 100, complex formation was nearly complete. The enthalpies $\Delta H_f(l)$ for reaction 1 in sulfolane and AN are given in Table III. The enthalpies $\Delta H_s(HR)$, corresponding to

$$HR(g) \rightarrow HR(l) \qquad (3)$$

were calculated by combining known heats of vaporization or sublimation and our heats of mixing of HR with the solvents; relevant enthalpies are listed in Table III.

Discussion

Although the discussion will focus on the enthalpies of association ΔH_f for reaction 1, it is interesting to look first briefly at the association constants K in Table I and their variation with the proton donor and the solvent. In sulfolane the order of increasing donor strength of HR is $HCCl_3 < HCH_3O < HOH \ll HC_6H_5O$. As the NMR method leads only to approximate values of K when these are large, ordering of the carboxylic acids is best deduced from K values in DMF and Me_2SO, as: $HCH_3CO_2 < HCH_2ClCO_2 \sim HCHCl_2CO < HCF_3CO_2$. The position of HC_6H_5O and HCl with respect to the carboxylic acid series is not exactly known.

That phenol is a stronger proton donor than water with respect to halide salts has already been shown in $CDCl_3$.[2] It is remarkable that association constants between water (or phenol) and Cl^- (tetraethylammonium chloride) are only slightly different in sulfolane and in $CDCl_3$ (or CH_2Cl_2).[2] A similar situation prevails for the association constants between $HCCl_3$ and Cl^- (tetrabutylammonium chloride) in sulfolane or AN,[15] and CCl_4.[15] a variety of causes[2] account for the minor influence of these solvents on the values of K. On one hand, the proton donors HR interact much more strongly with sulfolane or AN than with the chlorinated hydrocarbons. On the other hand, Cl^- is present as "free" anions in the DPA solvents and as ion pairs in the previous other solvents. Furthermore HR interacts, in these other solvents, with the chloride ion pair and may even give rise to several types of ion aggregates.[2] The effect of ionic association on complex formation between anions and water is being currently investigated through isopiestic measurements.[19]

The K values of carboxylic acids in Me_2SO and DMF show the expected increase with the acid strength of HR and a low sensitivity to the σ Hammett parameters. The variations of K from Me_2SO to AN for a given acid HR such as HCH_3CO_2 principally reflect the increasing interactions of HR with the solvent following the basicity order sulfolane $\sim$ AN $\ll$ DMF $<$ Me_2SO. The effect of the nature of ion X^- on its association constant K with a given donor HR has been examined for some common anions. Huyskens[6] found for K the order $NO_3^- \sim Br^- < Cl^-$ with benzoic acid in AN, and Kuntz[2] reported $ClO_4^- < I^- < SCN^- < Br^- < NO_3^- < Cl^- < SO_4^{2-}$ with phenol in CH_2Cl_2 in agreement with predictions from simple electrostatic theory. In the gas phase, K or rather ΔH appears to increase with the basicity of X^-.[8]

Looking now at the enthalpies of complex formation in Table III, we find that the order of increasing donor strength based on $\Delta H_f(l)$ in sulfolane is $HCCl_3 < HOH < HCH_3O \sim HCH_3CO_2 < HC_6H_5O < HCO_2H \sim HCF_3CO_2 \ll HCl$, whereas the order based on gas phase[8] $\Delta H_f(g)$ is $HOH < HCH_3O < HCCl_3 \sim HC_6H_5O < HCH_3CO_2 < HCl \ll HCO_2H$. The relationship between gas phase acidity of HR and $\Delta H_f(g)$ has already been discussed.[8] The different orders in both phases and the generally narrower range of variation of ΔH_f in the liquid phase are of course due to solvent effects on HR and $ClHR^-$.

We consider first the solvent effect on HR. $\Delta H_s(HR)$ which corresponds to $HR(g) \rightarrow HR(l)$ varies widely in sulfolane from a low of -5.8 for HCl, to highs of -13.4 for HCF_3CO_2 and -14.5 kcal mol^{-1} for HC_6H_5O. We also note in Table II that, for a given HR, $\Delta H_s(HR)$ in sulfolane and AN differ by less than 0.4 kcal mol^{-1} irrespective of the donor strength of HR. This means that the "hydrogen-bonding basicity" of both solvents are very close and that ΔH_s of a given solute is not very sensitive to the rather different physical properties of both solvents. On the contrary, the $\Delta H_s(HR)$ values for the carboxylic acids in DMF are 3-5 kcal mol^{-1} more exothermic than for AN or sulfolane, reflecting the stronger basicity of DMF.

We now turn to the solvent effect on $ClHR^-$. A simple thermodynamic cycle shows that

$$\Delta H_s(ClHR^-) - \Delta H_s(Cl^-) = \Delta H_f(l) + \Delta H_s(HR) - \Delta H_f(g) \quad (I)$$

Thus the solvation enthalpy of $ClHR^-$ in sulfolane can be calculated from our results and Kebarle's gas phase values[8] once the solvation enthalpy of Cl^- is known. This latter value can be taken from the solvation enthalpy of Cl^- in water and the enthalpy of transfer of Cl^- from water to sulfolane based on an extrathermodynamic assumption.[20] However, we have chosen to express $\Delta H_s(ClHR^-)$ with respect to $\Delta H_s(Cl^-)$ in the solvent; i.e., we assign $\Delta H_s(Cl^-) = 0$. The positive values found for $\Delta H_s(ClHR^-)$ and given in Table III merely indicate that $ClHR^-$ is less strongly solvated than Cl^-, partly because of its larger size. Although $ClHR^-$ becomes generally less strongly solvated when the size of HR increases, other more complex factors are obviously playing a part. For example, the lower value (stronger solvation) for $\Delta H_s(ClHC_6H_5O^-)$ is partly accounted for by stronger interactions between the benzene ring and the solvent as suggested by $\Delta H_s(CH_3OC_6H_5) = -10.4$ kcal mol^{-1} compared with a lower $\Delta H_s(CH_3OCH_3CO) = -7.9$ kcal mol^{-1}. The value +22.2 obtained for $\Delta H_s(ClHCO_2H^-)$ appears to be out of line and may warrant a check of the correspondingly high $\Delta H_f(g)$ for HR = HCO_2H.[21] Attempts were made to estimate some values of the "neutral contribution" to $\Delta H_s(ClHR^-)$ by taking ΔH_s for uncharged analogs of $ClHR^-$: $CH_3OC_6H_5$ ($\Delta H_s = -10.4$ kcal mol^{-1}) for $ClHOC_6H_5^-$, CH_3OCH_3CO ($\Delta H_s = -7.9$ kcal mol^{-1}) for $ClHOCOCH_3^-$, and CH_3OCH_3 (estimated $\Delta H_s = -6.5$ kcal mol^{-1}) for $ClHOCH_3^-$. By subtracting ΔH_s(neutr) from the $\Delta H_s(ClHR^-)$ values in Table III, the following "electrostatic contributions", to $\Delta H_s(ClHR^-)$ were obtained: $ClHOC_6H_5^-$ (+11.5 kcal mol^{-1}), $ClHOCOCH_3^-$ (+14.9 kcal mol^{-1}), and $ClHOCH_3^-$ (+9.9 kcal mol^{-1}). There is no apparent trend, but the values are too few and it may be that the three species are too dissimilar or that the analogs are not satisfactory.

Table IV. Enthalpy Changes, $\Delta H_f(l,g)$ (kcal mol^{-1}), for the Reaction $Cl^-(l) + HR(g) \rightarrow ClHR^-(l)$

HR	Sulfolane[a]	AN[b]	DMF[b,d]
$HCCl_3$	−10.9	−10.3	
HOH	−11.5	−10.6	
HC_6H_5O	−18.3	−16.3[c]	
HCH_3CO_2	−14.6	−13.3	−13.9
HCF_3CO_2	−17.4	−16.5	−17.2

[a] 30°C. [b] 25°C. [c] From calorimetric determinations using solid phenol and assuming an association constant $K \geq 100$. [d] Reference 12.

No evidence could be found through NMR and calorimetry for hydrogen bonding of Cl^- with two aromatic carbon acids, 1,3,5-trichlorobenzene in sulfolane, and toluene in AN, although ir work indicates hydrogen bonding between the aromatic hydrogens of the former donor and pyridine in CCl_4.[22] For toluene we attempted to estimate a value of $\Delta H_f(g)$ for the hydrogen-bond gas-phase enthalpy by assuming $-\Delta H_f(l) \leq 1$ kcal mol^{-1} and taking $\Delta H_s(ClH_3CC_6H_5^-) \sim \Delta H_s(ClHC_6H_5O^-)$. Equation I gave us $-\Delta H_f(g) \leq 11$ kcal mol^{-1} so that toluene is, not surprisingly, the poorest donor of those listed in Table III. A direct thermodynamic study of gas-phase hydrogen bonding between Cl^- and a series of carbon acids is in progress.[21]

Finally we compare the effect of the three solvents, sulfolane, AN, and DMF, on the enthalpy changes for the reaction $Cl^-(l) + HR(l) \rightarrow ClHR^-(l)$. In order to eliminate the solvent effect on HR, we calculated $\Delta H_f(l,g) = \Delta H_f(l) + \Delta H_s(HR)$; i.e., the enthalpy change for the reaction $Cl^-(l) + HR(g) \rightarrow ClHR^-(l)$. Results are given in Table IV. We note that, for a given donor HR, $\Delta H_f(l,g)$ varies but little from sulfolane to AN, and DMF. Similar results as yet unpublished were recently obtained for the $\Delta H_f(l,g)$ values of two other anion-molecule reactions, namely $Cl^-(l) + SbCl_5(g) \rightarrow SbCl_6^-(l)$[16] and $I^-(l) + I_2(g) \rightarrow I_3^-(l)$, taking place in five dpa solvents. The near-constancy of the $\Delta H_f(l,g)$ values of anion-molecule reactions[23] means that the difference between the enthalpies of transfer of a pair of anions, Cl^- and $ClHR^-$, for example, from one dpa solvent to another, varies little. This would of course be expected if the single anion enthalpies of transfer for dpa solvents were small. Single anion values[24] obtained from an extrathermodynamic assumption also point in this direction.

Acknowledgments. The financial assistance of the National Research Council in the form of a grant and a scholarship (C.L.) is gratefully acknowledged. We thank Professors E. M. Arnett, P. Kebarle, and I. D. Kuntz, Jr., for preprints and helpful correspondence.

References and Notes

(1) (a) A. Allerhand and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **85**, 1233 (1963); (b) M. M. Davis in "The Chemistry of Non-aqueous Solvents", Vol. III, J. J. Lagowski, Ed., Academic Press, New York, N.Y., 1970, Chapter 1, and references therein.

(2) (a) R. P. Taylor and I. D. Kuntz, Jr., *J. Am. Chem. Soc.*, **94**, 7963 (1972); *J. Phys. Chem.*, **74**, 4573 (1970); (b) I. D. Kuntz, Jr., and C. J. Cheng, *J. Am. Chem. Soc.*, in press.

(3) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **91**, 4621 (1969).

(4) M. K. Chantooni, Jr., and I. M. Kolthoff, *J. Am. Chem. Soc.*, **92**, 7025 (1970).

(5) Z. Pawlak, *Rocz. Chem.*, **46**, 249 (1972).

(6) D. J. Pirson and P. L. Huyskens, *J. Solution Chem.*, **3**, 503 (1974).

(7) E. M. Arnett, *Acc. Chem. Res.*, **6**, 404 (1973), and references therein.

(8) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **93**, 7139 (1971).

(9) R. L. Benoit and S. Y. Lam, *J. Am. Chem. Soc.*, **96**, 7385 (1974).

(10) R. L. Benoit, M. Rinfret, and R. Domain, *Inorg. Chem.*, **11**, 2603 (1972).
(11) R. L. Benoit and S. Y. Lam, *Can. J. Chem.*, **52**, 718 (1974).
(12) C. Louis, Ph.D. Dissertation, Université de Montréal, 1975.
(13) R. L. Benoit, A. L. Beauchamp, and R. Domain, *Inorg. Nucl. Chem. Lett.*, **7**, 557 (1971).
(14) (a) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **95**, 8539 (1973); (b) M. K. Chantooni, Jr., and I. M. Kolthoff, *J. Phys. Chem.*, **77**, 527 (1973).
(15) R. D. Green and J. S. Martin, *J. Am. Chem. Soc.*, **90**, 3659 (1968).
(16) R. Domain, Ph.D. Dissertation, Université de Montréal, 1975.
(17) (a) I. Wadsö, *Acta Chem. Scand.*, **20**, 544 (1966); (b) J. Konicek and I. Wadsö, *ibid.*, **24**, 2612 (1970).
(18) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds", Elsevier, New York, N.Y., 1950.
(19) E. M. Arnett, private communication.
(20) G. Choux and R. L. Benoit, *J. Am. Chem. Soc.*, **91**, 6221 (1969).
(21) P. Kebarle, private communication.
(22) A. Allerhand and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **85**, 1715 (1963).
(23) Some minor but significant variations of $\Delta H_{\mathrm{tr}}(\mathrm{l,g})$, for such anion–molecule reactions [and of corresponding ΔG_{tr}, see R. L. Benoit, A. L. Beauchamp, and M. Deneux, *J. Phys. Chem.*, **73**, 3268 (1969), for $\mathrm{Cl^-(l)} + \mathrm{AgCl}\downarrow \rightleftarrows \mathrm{AgCl_2^-(l)}$] are nevertheless observed for some common dpa solvents.
(24) B. G. Cox, G. R. Hedwig, A. J. Parker, and D. W. Watts, *Aust. J. Chem.*, **27**, 477 (1974).

Competition between Proton Transfer and Elimination in the Reactions of Strong Bases with Fluoroethanes in the Gas Phase. Influence of Base Strength on Reactivity

S. A. Sullivan[1a] and J. L. Beauchamp*[1b]

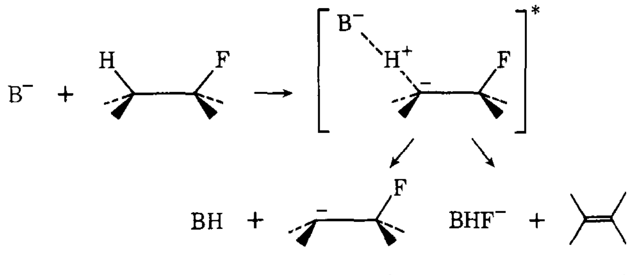
Contribution No. 5100 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125.

Received April 28, 1975

Abstract: Fluoroethanes react with strong bases in the gas phase by proton transfer, elimination of HF, and production of F^-. Ion cyclotron resonance spectroscopy has been used to examine the relative importance of these processes for a series of bases of varying strength, including NH_2^-, OH^-, CH_3O^-, $CH_3CH_2O^-$, $(CH_3)_2CHO^-$, $(CH_3)_3CO^-$, F^-, and CN^-. Reactant base strength is the principal factor determining product distributions. With decreasing base strength, the amount of proton transfer decreases relative to elimination. Observed proton transfer reactions establish limits for the acidities of the fluoroethanes. In addition, binding energies of F^- to the fluoroethanes, fluoroethylenes, and HF have been determined. With these thermochemical data, a satisfactory explanation of the effect of base strength on reactivity is provided by the application of straightforward concepts of unimolecular reaction kinetics.

With the development of ion cyclotron resonance spectroscopy (ICR), it has become possible to examine organic reaction mechanisms without solvent mediation. In particular, the result of a bimolecular encounter between a reagent ion and a neutral molecule can be observed. We have recently demonstrated, for example, that strong bases such as CH_3O^- can effect elimination reactions in the gas phase.[2] These studies are summarized in Scheme I. The interaction of a base with an acidic hydrogen of the fluoroalkane leads to the formation of a chemically activated intermediate which can decompose either by cleavage of the C-H bond (proton transfer) or by cis elimination with HF remaining bound to the attacking base. With several fluoroethanes F^- is also observed. It was proposed that this product results from the breakup of either the intermediate or ionic products in Scheme I rather than from a nucleophilic displacement reaction. The ionic products in Scheme I react further, transferring F^- to the neutral fluoroethane. When observed, the product F^- effects HF elimination from the neutral fluoroethane to form the bihalide ion FHF^-.

Scheme I



We wish to report an extension of the above studies in which reactivity has been examined with a range of gases of varying strength. With different bases it is expected that the internal excitation of the reaction intermediate, as well as the exothermicities of the different reaction pathways, can be varied significantly. The reactants selected include NH_2^-, OH^-, CH_3O^-, $CH_3CH_2O^-$, $(CH_3)_2CHO^-$, $(CH_3)_3CO^-$, F^-, and CN^-, which cover a wide range of base strengths (Table I).

Experimental Section

Experiments were performed using both a modified Varian V-5900 ICR spectrometer with a 9-in. magnet system and a spectrometer, built in this laboratory, incorporating a 15-in. magnet and capable of operating up to m/e 750. The general aspects of instrumentation and experimental techniques of ICR have been detailed elsewhere.[3]

In a typical experiment the precursor of the reagent base was admitted to the analyzer and maintained at a constant pressure. The fluoroethane was subsequently added through another inlet so that its pressure could be varied independently. Relative ion intensities were measured as a function of the fluoroethane partial pressure. To determine the relative acidities of the fluoroethanes, a reagent base is added to a mixture of two ethanes. The fluoroethyl carbanions are formed and their reactions with neutral ethanes can be observed. These experiments were performed using three inlets which allowed independent pressure variation of all components. Pressure meaurements were made using a Schulz-Phelps ion gauge, calibrated against a MKS Baratron Model 90H1-E capaci-