Can. J. Chem. Downloaded from www.nrcresearchpress.com by CLEMSON UNIVERSITY on 11/13/14
For personal use only.

Hydrogen bonding of O—H and C—H hydrogen donors to Cl^-. Results from mass spectrometric measurements of the ion–molecule equilibria $RH + Cl^- = RHCl^-$

M. A. FRENCH, S. IKUTA,[1] AND P. KEBARLE

Department of Chemistry, University of Alberta, Edmonton, Alta., Canada T6G 2G2

Received November 20, 1981

M. A. FRENCH, S. IKUTA, and P. KEBARLE. Can. J. Chem. **60**, 1907 (1982).

Equilibrium constants K_1 for reaction [1] $RH + Cl^- = RHCl^-$ in the gas phase were measured with a high pressure mass spectrometer under chemical ionization conditions. Data for some 40 compounds RH are presented. It is found that the binding free energies ($-\Delta G_1^\circ = RT \ln K_1$) for RH = oxygen acids increase with the gas phase acidity of RH. The strongest bonds are formed with strong acids like HCO_2H, CH_3CO_2H, and phenol. Water and alkyl alcohols give much weaker interactions. A simple relationship between gas phase acidity and binding free energy does not occur for RH = carbon acids. Carbon acids like cyclopentadiene, whose high gas phase acidity is largely due to charge delocalization by conjugation in the completed anion, do not give Cl^- adducts with stability commensurate with the acidity. A relationship between gas phase acidity and binding energy is found for carbon acids with carbonyl groups and for the substituted toluenes. Molecular orbital calculations with the STO-3G basis set provide insights to the bonding occurring in $RHCl^-$. For all cases investigated, hydrogen bonding to Cl^- provides the most stable structure. Generally the hydrogen bond occurs through the hydrogen which has the highest net positive charge. The hydrogen bond strength is found approximately proportional to this positive charge. Another proportionality is found between the charge transferred from Cl^- to RH, on formation of $RHCl^-$, and the strength of the hydrogen bond.

M. A. FRENCH, S. IKUTA et P. KEBARLE. Can. J. Chem. **60**, 1907 (1982).

On a mesuré la constante d'équilibre K_1 de la réaction [1] $RH + Cl^- = RHCl^-$ en phase gazeuse à l'aide d'un spectromètre de masse à haute pression et à ionisation chimique. On présente les données relatives à 40 composés du type RH. On a trouvé que les énergies libres de liaison, ($-\Delta G_1^\circ = RT \ln K_1$), dans les cas où RH = acides oxygénés, augmentent avec l'acidité de la phase gazeuse de RH. Les liaisons hydrogènes les plus fortes s'établissent avec les acides forts, tels le HCO_2H, le CH_3CO_2H et le phénol. L'eau et les alcools alkylés donnent lieu à des interactions beaucoup plus faibles. On n'obtient pas de relation simple entre l'acidité de la phase gazeuse et l'énergie libre de liaison dans les cas où RH = acides carbonés. Les acides carbonés du type cyclopentadiène, dont la forte acidité en phase gazeuse est due à une grande délocalisation de la charge par conjugaison de l'anion complété, ne donnent pas d'adduits avec Cl^- qui auraient une stabilité proportionnelle à l'acidité. On a trouvé une relation entre l'acidité de la phase gazeuse et l'énergie de liaison dans le cas des acides carbonés ayant des groupes carbonylés et dans le cas des toluènes substitués. Les calculs d'orbitales moléculaires avec l'ensemble de base STO-3G fournissent des informations sur la liaison qui s'établit dans $RHCl^-$. Dans tous les cas étudiés, la liaison hydrogène avec Cl^- conduit à la structure la plus stable. En général, la liaison hydrogène s'établit par l'intermédiaire de l'hydrogène qui a la plus forte charge positive totale. On a trouvé que la force de la liaison hydrogène est presque proportionnelle à sa charge positive. On a trouvé une autre proportionnalité entre la charge transferrée du Cl^- au RH lors de la formation de $RHCl^-$ et la force de la liaison hydrogène.

[Traduit par le journal]

Introduction

The association of molecules with negative ions is of interest in several disciplines. Strongly held adducts involving negative ions and acids like HNO_2, HNO_3, HCl, and HBr occur in the earth's atmosphere (1). The adducts of various molecular species of Cl^- can be used for analytical purposes in negative ion chemical ionization mass spectrometry (2). Hydrogen bonded complexes between neutral hydrogen donors and negative ions have been observed and studied in aprotic solvents (3, 4). In a more general sense, information on the bonding of various neutral compounds to negative ions like Cl^-, etc. belongs to the large area of hydrogen bonding, since the interactions turn out to be predominantly hydrogen bonding ones. Improved understanding of the nature of bonding is of significance also to ion solvation and ion stabilization in different environments. For example, complexing positive ions with suitably designed compounds like crown ethers or cryptates (5) facilitates their passage into hydrophobic media, biological membranes, or liquid membranes in ion selective electrodes (6). Less developed is the design and synthesis of similar compounds which are to complex selectively with negative ions.

The present work provides information on the binding free energies of some 38 compounds with Cl^-. The information is obtained from the measurement of the ion–molecule equilibria [1] with a pulsed electron beam high pressure mass spectrometer. Measurement of the equilibrium con-

---

[1] Permanent address: Department of Chemistry, Tokyo Metropolitan University, Fukasawa, Setagaya-ku, Tokyo 158, Japan.

0008-4042/82/151907-12$01.00/0

©1982 National Research Council of Canada/Conseil national de recherches du Canada

Can. J. Chem. Downloaded from www.nrcresearchpress.com by CLEMSON UNIVERSITY on 11/13/14
For personal use only.

stants K_1 at a given constant temperature T leads to the free energy change $\Delta G_1^0 = -RT \ln K_1$. Measurement of the temperature dependence of K_1 leads also, via van't Hoff plots, to ΔH_1^0 and ΔS_1^0.

[1] $Cl^- + RH = RHCl^-$

[2] $R_0^- + RH = R_0H + R^-$

Several determinations of equilibria [1] have been published in previous reports from this laboratory. Measurements involving RH (HCOOH, CH_3COOH, C_6H_5OH, $HCCl_3$, $(CH_3)_3COH$, CH_3OH, H_2O) showed (7, 8) that the strong hydrogen bond $Cl^- \cdot\cdot HR$ (i.e. the chloride affinity of HR) increases approximately linearly with increase of the phase acidity of HR. A good linear relation is obtained for the case where the acids are more closely related, i.e. substituted phenols (9).

The early (1, 2) comparisons of chloride affinity and gas phase acidity were made on the basis of very incomplete and somewhat questionable data for the gas phase acidities of the RH compounds involved. Fortunately, since then, abundant data on gas phase acidities have become available from measurements in this (10) and other laboratories (11) of proton transfer equilibria [2] which provide accurate relative gas phase acidities. In the present work comparisons between the chloride affinities and gas phase acidities of the oxyacids are based on these newer and more accurate acidity data. The gas phase acidities of many nitrogen and carbon acids were part of the recent acidity determinations (10, 11). While only a few determinations of the chloride affinities of nitrogen acids have been made, it is to be expected that the relationships observed for oxygen acids will approximately hold also for nitrogen acids. The case of the carbon acids is quite different. Taking the term carbon acids in the broadest sense, carbon acids involve C—H hydrogens of all possible bonding environments, i.e. aromatic C—H hydrogens, allylic hydrogens, etc. Evidently, for some of the compounds involved, bonding to Cl^- may not be occurring via a hydrogen bond, but by an electrostatic interaction with a whole group of atoms or by an interaction with a particular carbon atom, i.e. by the formation of a σ complex. Even when the most stable adduct is hydrogen bonded, the parameters determining the strength of the bond are not so easily deduced. It is likely that a simple relationship with the gas phase acidity cannot be expected. For example, cyclopentadiene is a rather strong gas phase acid, its gas phase acidity is comparable to that of p-NH_2,phenol (10), yet this compound cannot be expected to have a high chloride affinity. The high acidity of the cyclopentadiene is largely due to the charge delocalization in the anion $C_5H_5^-$ in which the charge is evenly distributed on all five CH groups. Evidently, a compound whose gas phase acidity is achieved largely through delocalization of an electron pair from a former C—H bond cannot compete in hydrogen bonding with a compound whose acidity is largely due to a charge separation induced by an electronegative atom like oxygen.

In order to explore the chloride affinities of carbon acids, a number of determinations of equilibria [1] with RH = carbon acids were made in the present work. The measurements provide very useful thermochemical data, but of course no direct structural information. Considerable help in the bonding analysis can be obtained from molecular orbital calculations (STO-3G) of the energies of possible structures of the complexes $RHCl^-$.

Experimental

The measurements of the equilibrium constants K_1 were made with a pulsed electron beam high ion source pressure mass spectrometer. The apparatus was the same as that used in earlier work on Cl^- and phenols (9). It differed from that used in the earliest work (7) where pulsing of the electron beam was not employed. In the earliest work (7) neat gas RH was used in the ion source at pressures of 0.6 to 2 Torr. The use of the neat gas, in some cases, may lead to incorrect measurements due to unimolecular or collision-induced decomposition of the ion–molecule adduct in the mass analysis system (12). Therefore the present measurements were executed with methane as major gas. Generally, the methane contained 0.1 to 5% RH. The total ion source pressure was in the range 1–4 Torr.

The measurements with formic acid and phenol made in the earlier work (7) were repeated. The equilibrium constants for phenol at different temperatures as a function of phenol partial pressure are shown in Fig. 1. The equilibrium constants observed are seen to be quite independent of the phenol partial pressure. The phenol pressure is varied by a factor of 4. At low temperatures, where K_1 is large, low phenol partial pressures are used in order not to let the ion ratio $RHCl^-/Cl^-$ become much larger than unity.

van't Hoff plots for three determinations (HCOOH, PhOH, acetone) are shown in Fig. 2. The agreement with the earlier results for HCOOH is fairly good. The data points for the two determinations are very close; however, a deviation of the older data points (7) (see Fig. 2) at high temperature (low K_1) leads to a larger slope, i.e. a larger $-\Delta H_1$, for the earlier work. The present data, obtained with improved experimental conditions and extending over a wider temperature range, are believed to be the more reliable set. A considerably larger deviation between present and earlier data is observed for phenol (see Fig. 2). This disagreement must be due to some specific problem connected with the use of neat phenol in the earlier work. The very high molecular weight of phenol and its strong adsorption on metal surfaces may have led to an unusually high residual gas pressure in the acceleration and mass analysis system. Recent work (12, 13) has shown that under such conditions significant collision-induced decomposition (or $RHCl^-$ in the present case) can reduce the observed ion ratio $RHCl^-/Cl^-$. A recent redetermination[2] of the equilibrium $Cl^- + H_2O = Cl^-H_2O$, with methane as major gas, led to results in agreement with the earlier work (8b) which was undertaken with neat water. This observa-

---

[2] T. F. Magnera and P. Kebarle. Kinetics of the hydration of the Cl^- ion. To be published.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by CLEMSON UNIVERSITY on 11/13/14
For personal use only.

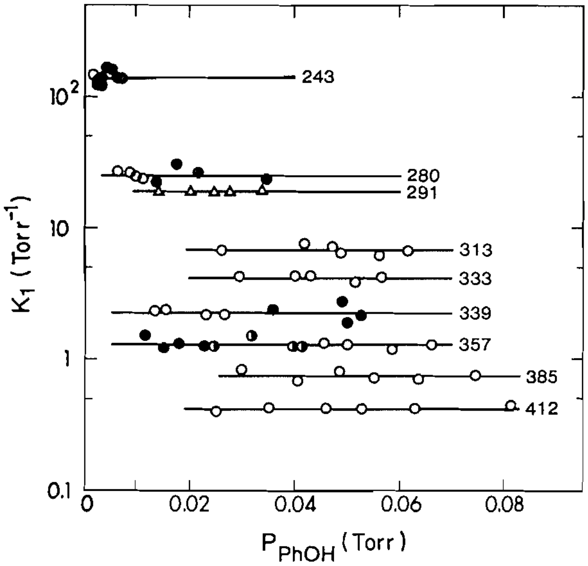


FIG. 1. Measured equilibrium constants for reaction: $Cl^- + PhOH = PhOHCl^-$ at different constant temperatures given in degrees C. Equilibrium constant is found independent of phenol pressure. Experiments performed in the presence of a third gas methane at 1 to 5 Torr pressure. Different symbols for same temperature correspond to different ratios of phenol to methane.

tion also suggests that phenol represented a special problem in the earlier measurements. As will be shown in the next section, the present result for phenol is in better accord with theoretical predictions.

In order to cover a large number of compounds RH, determinations of the equilibrium constant K_1 were made only at one temperature. These data, shown in Figs. 3 and 4, will be discussed in the next section.

Calculations

The ΔE(STO-3G) data used in this work were obtained by calculating the total energies of the reactants in reaction [1] and obtaining ΔE from : $E(RHCl^-) - E(Cl^-) - E(RH)$. The STO-3G calculations of the total energies E were performed with the Gaussian 70 and Hondo 5 programmes based on Pople's (14) STO-3G minimal basis set. The geometries used were standard geometries from Pople and Gordon (14) except: methanol, Harmony *et al.* (15*a*); acetone, J. E. Bel Bene (15*b*); pyrrole, Clementi *et al.* (16*a*); formic acid, Clementi *et al.* (16*b*). In the structures $RHCl^-$ shown in Fig. 6, only a few of the bond distances were optimized. These are shown in Table 3. In general, first the Cl^- distance to the rigid R—H was optimized. Then for a fixed Cl^- distance the O—H distance or C—H distance for oxygen or carbon acids was optimized.

Results and discussion

General description of results

The present results consist of determinations of the equilibrium constants K_1 for the reaction [1], $Cl^- + RH = RHCl^-$. The experimental data are summarized in Figs. 2, 3, and 4. Shown in Fig. 2 are the few cases (formic acid, phenol, acetone) for which the temperature dependence of the equilibrium constants was measured. The resulting van't Hoff plots permit the determination of ΔH°_1 and ΔS°_1. In order to cover a large number of compounds, the remaining equilibrium constant determinations were made at a single temperature. Figure 3 summarizes the determinations at room temperature. This group consists of 18 compounds and covers equilibrium constants from $K_1 \approx 0.5$ to $K_1 = 1000$ (Torr^{-1}). Equilibrium constants much larger than 1000 are difficult to determine with the present apparatus. Therefore several equilibria of interest, involving more strongly bonding compounds, were measured at a temperature of 148°C. These are shown in Fig. 4.

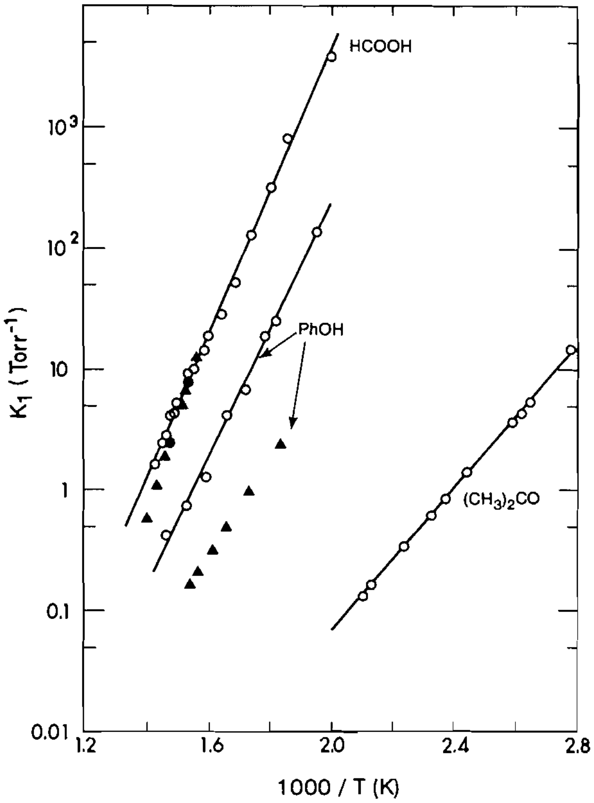


FIG. 2. van't Hoff plots for equilibria: $RH + Cl^- = RHCl^-$. ○, present results with CH_4 as major gas. ▲, Yamdagni and Kebarle (7) with use of neat RH. ●, present results with neat formic acid.

Tables 1 and 2 summarize the available data. Table 1 contains the compounds for which van't Hoff plots are available. Present and previous determinations involving Cl^- (7–9, 17) are included. Table 2 gives the free energy change $\Delta G^\circ_1 = -RT \ln K_1$ at 300 K of all the compounds for which

Can. J. Chem. Downloaded from www.nrcresearchpress.com by CLEMSON UNIVERSITY on 11/13/14
For personal use only.

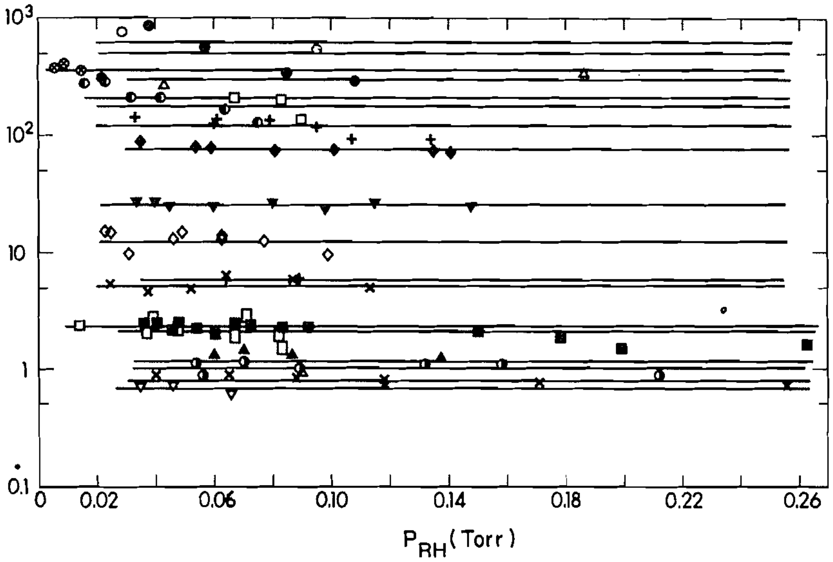


FIG. 3. Measured equilibrium constants for reaction [1]: $Cl^- + RH = Cl^- \cdot RH$ at 26°C where RH is ○, acetone; ●, *m*-difluorobenzene; ⊗, *p*-nitrotoluene; △, diphenylmethane; ◐, iodobenzene; □, nitrobenzene; +, bromobenzene; ◆, chlorobenzene; ▼, fluorobenzene; ◇, cumene; +, *n*-propylbenzene; +, ethylbenzene; ⊡, mesitylene; ▯, *m*-xylene; ▲, toluene; ◑, *p*-xylene; ×, benzene; ▽, 1,4-pentadiene.

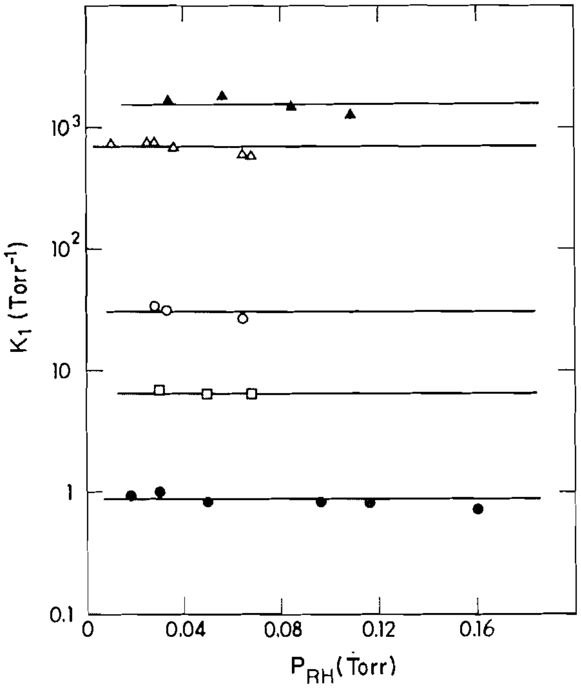


FIG. 4. Measured equilibrium constants for reaction [1]: $RH + Cl^- = RHCl^-$ at 148°C, where RH is: pyrrole ▲; acetylacetone △; phenylacetone ○; acetopheonone □; and acetone ●.

determinations are available from the present and previous work. For the compounds shown in Fig. 4, determinations of the equilibrium constant K_1 are available only at 148°C. In order to obtain the free energy change ΔG_1°, at room temperature, one requires the entropy change ΔS_1°. We made a rough estimate of ΔS_1° on the basis of the results in Table 1. These indicate that $-\Delta S_1^\circ$ decreases approximately with decreasing $-\Delta H_1^\circ$. The compounds in Fig. 1 include acetone, whose $\Delta S_1^\circ = -19.6$ cal K^{-1} was measured. The compounds in Fig. 4, which include acetone, fall in a not too broad bond strength range. Therefore a constant value of $\Delta S_1^\circ = -20$ cal K^{-1} was assumed for all of them. The ΔG_1° data in Table 2 for these compounds are obviously only estimates.

Hydrogen bonding of Cl^- to oxygen acids

As was mentioned in the introduction, earlier work (6–9, 17) showed that the hydrogen bond strength $RH \cdot\cdot Cl^-$ increases as the gas phase acidity of RH increases. Most of the compounds involved in that relationship were oxygen acids.

The correlation was suggested before accurate and plentiful data for gas phase acidities were available. Fortunately, the present data can be examined with the help of recent comprehensive determinations of gas phase acidities (10, 11). The hydrogen bonds to Cl^- ($-\Delta G_1^\circ$) of oxygen acids are shown in Fig. 5 plotted versus the corresponding gas phase acidities. The data fit quite well into a smooth curve which shows that the hydrogen bond free energies decrease with decrease of acidity of RH. It is interesting to note that the (negative) slope decreases gradually, i.e. the changes of hydrogen bonding with acidity are largest for the strongest

Can. J. Chem. Downloaded from www.nrcresearchpress.com by CLEMSON UNIVERSITY on 11/13/14
For personal use only.

TABLE 1.[a] Thermodynamic data

RH	$-\Delta G^0_1(300,\text{g})$	$-\Delta H^0_1(\text{g})$	$-\Delta S^0_{1(\text{g})}$	Reference[b]	$-\Delta H_{1(\text{sl})}$[c]	$-\Delta H_{\text{sl}}(\text{RH})$[d]	ΔH_4[e]
HCOOH	20.1	27.4	24.5	—	4.0	11	12.4
Phenol	19.2	26.0	25.0	—	3.7	14.6	7.7
HCl	16.7	23.7	23.5	8	8.1	5.8	9.8
CH_3OH	9.8	14.2	14.8	8	3.2	7.5	3.5
CH_3CN	9.2	13.4	14.3	8	—	—	—
HOH	8.2	13.1	16.5	8	2.6	8.9	1.6
Acetone	7.9	13.7	19.6	—	—	—	—

[a] Data relate to reaction [1]: $RH + Cl^- = RHCl^-$. The abbreviation g stands for reaction in the gas phase, sl for reaction in solution. ΔG^0 and ΔH^0 are given in kcal mol^{-1}, ΔS in cal K^{-1}, standard state 1 atm. The errors are estimated at ± 2 kcal/mol for $\Delta H^0_{(\text{g})}$ and $\Delta G^0_{(\text{g})}$ and ± 5 cal K^{-1} for $\Delta S^0_{(\text{g})}$.

[b] Literature reference for gas phase reaction [1]; where no reference is given, determination was made in present work.

[c] $\Delta H_{1(\text{sl})}$ for sulfolane from Benoit and co-workers (4).

[d] $\Delta H_{\text{sl}}(\text{RH})$ corresponds to enthalpy change for reaction $HR_{(\text{g})} \rightarrow HR_{(\text{sl})}$, where solvent is sulfolane. Data from Benoit and co-workers (4).

[e] $\Delta H_{\text{sl}}(Cl^-HR) - \Delta H_{\text{sl}}(Cl^-) = \Delta H_4$ is obtained from cycle [2] and eq. [4]. $\Delta H_{\text{sl}}(Cl^-HR)$ corresponds to enthalpy change for reaction $ClHR^-_{(\text{g})} \rightarrow ClHR^-_{(\text{sl})}$, where solvent is sulfolane. $\Delta H_{\text{sl}}(Cl^-)$ for same process but involving Cl^-.

TABLE 2. Binding free energies ΔG^0_1 of Cl^- to compounds RH

RH	$-\Delta G^0_1(300)$[a]	ΔH_D[b]	RH	$-\Delta G^0_1(300)$[a]	ΔH_D[b]
p-CN,phenol	26.0[c]	332.1[j]	*p*-NO_2,toluene	7.5[d]	
p-Cl,phenol	20.8[c]	343.2[j]	Diphenylmethane	7.4[d]	364.5[k]
HCO_2H	20.1[d]	345.2[j]	Anisole	7.3[d]	
p-F,phenol	19.3[c]	347.2[j]	I-benzene	7.2[d]	
CH_3CO_2H	~17.3[c]	348.5[j]	NO_2-benzene	7.1[d]	
Phenol	17.2[c]	349.8[j]	Br-benzene	6.8[d]	
HCl	16.7[f]	333.6[j]	Cl-benzene	6.5[d]	
p-Me,phenol	16.6[c]	351.1[j]	F-benzene	5.9[d]	
Pyrrole	~14.0[g]	359.2[j]	*i*-Pr-benzene	5.5[d]	377.5[k]
$(CH_3CO)_2CH_2$	~13.4[g]	343.7[j]	*n*-Pr-benzene	5.0[d]	
*t*BuOH	11.1[e]	374[k]	Et-benzene	5.0[d]	378.3[k]
$PhCH_2COCH_3$	~10.7[g]	351.8[j]	Mesitylene	4.5[d]	
$CHCl_3$	~10.3[h]		*m*-Xylene	4.4[d]	
MeOH	9.8	380[k]	Triphenylmethane	4.1[d]	
MeCOPh	~9.5[g]	363[j]	Toluene	4.0[d]	379[k]
MeCN	8.4[h]	373.5[j]	*p*-Xylene	3.9[d]	380.5[k]
HOH	8.2[i]	390.8[k]	Benzene	3.8[d]	
Me_2CO	7.9[d]	370[j]	1,4-Pentadiene	3.7[d]	
m-diF,benzene	7.7[d]		Cyclopentadiene	<2.5[d]	356[j]

[a] Free energy change at 300 K for gas phase reaction $Cl^- + RH = RHCl^-$ in kcal/mol, standard state 1 atm.

[b] Deprotonation enthalpy corresponding to gas phase reaction $RH = R^- + H^+$. ΔH_D decreases with increase of gas phase acidity.

[c] From ref. 9 and phenol determination present work.

[d] Present work.

[e] Present work and ref. 7.

[f] Reference 17.

[g] Present work, estimate of $\Delta G^0(300)$ from single determination at 421 K (see Fig. 4).

[h] References 7 and 8.

[i] Reference 8 and footnote 2.

[j] Reference 10.

[k] Reference 11.

acids for which, one could assume, the largest degree of proton transfer to Cl^- occurs. This behavior is closely analogous to that observed in an earlier series (18) where the acids were oxonium and ammonium ions (H_3O^+, $EtOH_2^+$, $MeCO_2H_2^+$, NH_4^+, pyrridine H^+, etc.) and the proton acceptor was H_2O. In that case also, the slope was largest for the strongest acids (H_3O^+, $EtOH_2^+$) and decreased as the acids became weaker (pyridinium ions).

When the compounds were closely related, as is the case for the substituted pyridinium ions, the relationship between hydrogen bond energy (to H_2O) and acidity of the hydrogen donor was close to linear (18). It was also found that the hydrogen bond energies were proportional to the net positive charge on the acidic hydrogen of the pyridinium ions. The net positive charge was obtained from Mulliken electron population analysis with STO-3G basis sets by Reynolds *et al.* (19). These authors had shown that the acidity of the pyridinium ions is linearly related to the net atomic charge in the acidic hydrogen. Thus the relationship between hydrogen bond and net atomic charge could have been anticipated, once it was shown that the hydrogen bond energy increases with acidity.

It is interesting to note that the situation is exactly analogous for substituted phenols and Cl^-.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by CLEMSON UNIVERSITY on 11/13/14
For personal use only.

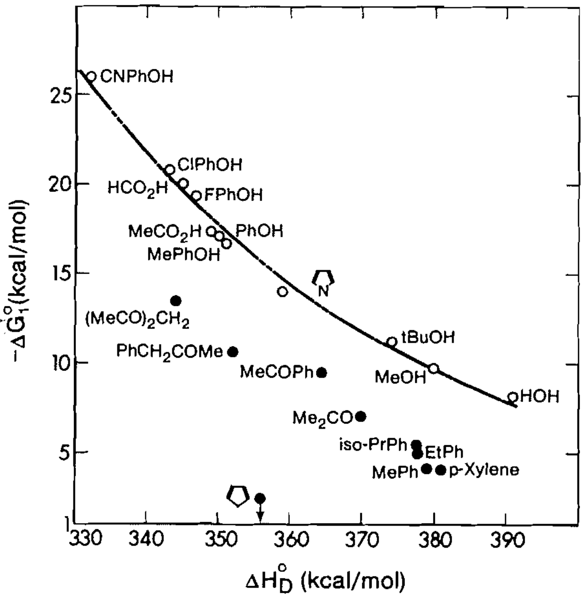


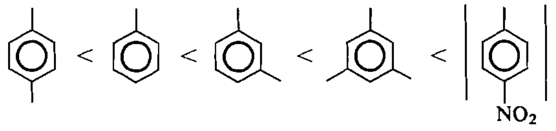
FIG. 5. Plot ΔG_1° for gas phase reaction ($RH + Cl^- = RHCl^-$) versus gas phase acidity of RH. ○ RH are oxygen acids (and pyrrole); ● RH are carbon acids. The gas phase acidity is expressed as ΔH_D°, the deprotonation energy corresponding to enthalpy change for reaction $RH = R^- + H^+$. The gas phase acidity increases as ΔH_D° decreases. The RH—Cl^- binding free energies ($-\Delta G_1^\circ$) of the oxygen acids fit on a common curve. The binding energy increases as the acidity of RH increases. The carbon acids (except cyclopentadiene) also seem to fit on a common curve. Data in Fig. 5 are also given in Table 2.

There is a close to linear relationship between the hydrogen bond in $RHCl^-$ and the acidity of the phenols (see Fig. 5 and Fig. 3, ref. 9). The acidities and net atomic charges on the acidic hydrogen of substituted phenols have been calculated by Hehre *et al.* (20). These data, when plotted, demonstrate that a good linear dependence exists between the calculated acidity of the phenols and the net atomic charge on the acidic hydrogen. There is quite good agreement between the STO-3G calculated (20) and the experimental (21, 22) acidities of the substituted phenols. Since there is a near linear relationship between acidity and hydrogen bonding with Cl^-, it follows that the hydrogen bond energy in the phenol Cl^- adducts is linearly related to the net atomic positive charge on the acidic hydrogen of the phenols.

Hydrogen bonding of Cl^- to carbon acids

The bonding free energies $-\Delta G_1^\circ$ for Cl^- association to carbon acids RH are shown in Fig. 5. None of these compounds falls on the correlation curve of the oxygen acids. All carbon acids have bonding free energies which are considerably lower than those for oxygen acids of the same gas phase acidity. The lowest chloride affinity is observed for cyclopentadiene (Fig. 3). The gas phase acidity for this compound is close to that of phenol and thus rather high. As already mentioned in the Introduction, the reason for the complete lack of correlation between acidity and chloride affinity in cyclopentadiene is easy to understand. The high acidity of cyclopentadiene is mostly due to the large stabilization by charge delocalization in the fully developed anion, in which each CH group carries one fifth of the negative charge. This stabilization is not available in the cyclo-$C_5H_6Cl^-$ adduct.

The remaining carbon acids (Fig. 5) seem to fall on a common curve which indicates a correlation between gas phase acidity and chloride affinity. For example, the chloride affinity order of the alkyl substituted toluenes: *p*-xylene, toluene, ethylbenzene, isopropylbenzene follows exactly the order of the gas phase acidities. For some of the toluenes, whose chloride affinities were measured in the present work, gas phase acidities are not available. However the acidity order can be inferred. For the series:



data from Table 2 show that the chloride affinities increase in the given orer. The gas phase acidities probably change also in the same order. The acidity order *para*-xylyl < toluene is experimentally observed. Methyl substitution on the aromatic ring, in *para* and *meta* position of phenols, leads to a decrease of acidity; however, the decrease is lower for the *meta* substituent (4, 12). This difference is expected because the π-like electron donation, from *para* methyl in the anion, brings destabilizing negative charge closer to the oxi group than is the case for the *meta* substituent. In the methyl substituted toluenes, *meta* substitution might in fact be slightly acidifying, since the favorable increase of the polarizability may be the overriding effect. This would lead to an acidity order which is the same as that shown above for the chloride affinities. The higher acidity for *p*-nitrotoluene is of course also expected.

The correlation of the chloride affinity with the gas phase acidity for the substituted toluenes and the carbonyl carbon acids (see Fig. 5) suggests that the chloride adducts of these compounds involve hydrogen bonding of the chloride to the most acidic hydrogen, i.e. the hydrogen that would be involved in the acid dissociation. In the next section, STO-

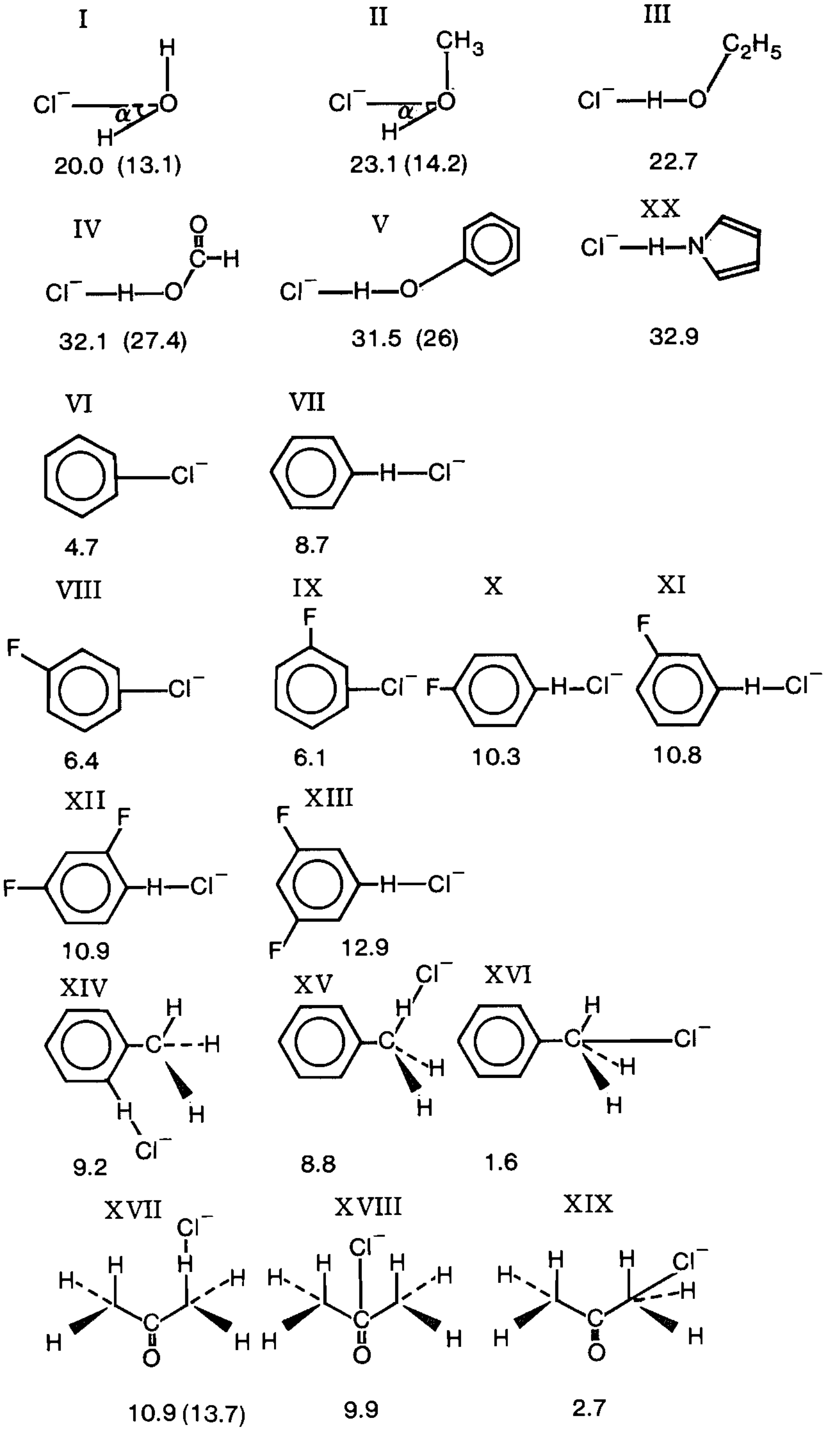


FIG. 6. Results from STO-3G calculations. The $-\Delta E$(STO-3G) calculated for the reaction [1]: $RH + Cl^- = RHCl^-$ is given under the specific structure of $RHCl^-$. Whenever available, the ΔH_1^0 measured experimentally are also given, these values are shown in brackets. Both results are in kcal/mol. In all structures shown, Cl^- and the major bond frame of RH are in the same plane. For example, in the substituted benzenes Cl^- and the benzene ring are in the same plane; in acetone, the Cl^- is in the plane of the C—CO—C bonds. Other details of the calculations are given in Table 3.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by CLEMSON UNIVERSITY on 11/13/14
For personal use only.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by CLEMSON UNIVERSITY on 11/13/14
For personal use only.

TABLE 3. Results from STO-3G calculations for strucutres $RHCl^-$

$(RHCl^-)^a$		$R(O—Cl)^b$	$R(O—H)^b$	α	$q(Cl^-)^c$
Cl^-HOH	I	2.934	1.005	6.2^0	−0.901
Cl^-HOCH_3	II	2.887	1.015	3.3^0	−0.880
$Cl^-HOC_2H_5$	III	2.889	1.016	2.4^0	−0.879
$Cl^-HOC_6H_5$	V	2.830	1.030	(0)	−0.835
Cl^-HOCOH	IV	2.795	1.030	(0)	−0.823
		$R(Cl^-..C)$	$R(C—H)$		
$Cl^-H—C_6H_5$	VII	3.203	(1.084)		−0.940
$Cl^-H—C_6H_4F$	XI	3.186	(1.084)		−0.939
$Cl^-H—C_6H_3F_2$	XIII	3.146	(1.084)		−0.930
$Cl^-CH_3HH_5$	XIV	3.227	1.113		−0.936
	XV	3.26	(1.113)		−0.944
$Cl^-CH_3COCH_3$	XVII	3.275	(1.086)		−0.952
	XVIII	3.67	—		−0.939
	XIX	3.54	—		−0.999

[a] Roman numerals correspond to structures shown in Fig. 6.

[b] Distance in Angstrom, distances shown without brackets were optimized, those with brackets were not optimized. For further details see section on calculations.

[c] Net atomic charge on Cl in $RHCl^-$. Charge on separated Cl^- is −1.0.

3G calculations are used to explore further the nature of the bonding that occurs in the adducts $RHCl^-$.

Comparison of chloride affinities with results from STO-3G calculations

The results of the STO-3G calculations are summarized in Fig. 6 and Table 3. Some details concerning the calculations are given in the section Calculations.

The first five structures in Fig. 6 deal with the bonding of Cl^- to the oxygen acids (HOH, $HOCH_3$, HOC_2H_5, HOPh, and HOCOH). Given in the figure are the STO-3G calculated binding energies and the experimentally determined ΔH values. Comparison between these two sets of results shows that the $-\Delta E$(STO-3G) are considerably larger than the experimental $-\Delta H$ values. The difference is most pronounced for the weak acids, HOH and $HOCH_3$. The calculated ΔE are closer to the experimental ΔH for the strong acids, phenol and formic acid.

It is well known that the basis set of STO-3G is too small and does not provide reliable stabilization energies even in the absence of electron correlation. Much closer agreement with the experimental result for Cl^-HOH, $\Delta H_1 = -13.1$ kcal/mol, has been obtained by Clementi and co-workers (23) who, using a large basis set, complete geometry optimization, correlation binding, and zero point difference correction, calculated $\Delta H_1 = -11.4$ kcal/mol. Kollman and Kunz (24), using the 431-G basis set, have obtained $\Delta E_1 = -19.9$ kcal/mol for the same comound, a value not significantly better than the $\Delta E_1 = -20$ kcal/mol obtained in the present work with the smaller STO-3G basis set. While the STO-3G basis set does not provide reliable absolute binding energies, the relative ordering of the binding energies is generally reliable. For example, the right order is predicted for the series HOH, CH_3OH, PhOH, and HCO_2H (see Fig. 6). However, when the differences are very small, the predicted order cannot be trusted. Thus the slightly weaker binding predicted for ethanol relative to methanol is probably wrong, since a slightly stronger bonding for ethanol can be expected on the basis of the higher gas phase acidity of ethanol. The STO-3G energies for the isodesmic reactions are found to be fairly close to the observed enthalpy changes. Three examples are given below, where the energy changes quoted are in kcal/mol. It is probably safe to assume that STO-3G also gives approximately the correct chloride affinity ordering the approximate chloride affinity differences for the other structures given in Fig. 6.

Reaction	ΔE(STO-3G)	ΔH^0	$\Delta G^0(300)$
$Cl^-HOH + CH_3OH = Cl^-CH_3OH + HOH$	−3	−1.1	−1.6
$Cl^-CH_3OH + HCO_2H = Cl^-HCO_2H + CH_3OH$	−9	−13.2	−10.3
$Cl^-PhOH + HCO_2H = Cl^-HCO_2H + PhOH$	−0.6	−1.4	−2.9

The results for structures VI and VII show that stronger bonding with benzene is obtained in the hydrogen bonding position VII. The experimental ΔG_1^0, for benzene is −3.8 kcal/mol (Table 2). Assuming the ΔS_1^0 is in the neighbourhood of -15 cal K^{-1} mol^{-1} one obtains, from $\Delta G = \Delta H -$

Can. J. Chem. Downloaded from www.nrcresearchpress.com by CLEMSON UNIVERSITY on 11/13/14
For personal use only.

$T\Delta S$, an estimate of $\Delta H_1^0 \approx -8$ kcal/mol. This value is close to the STO-3G result of 8.7 kcal mol^{-1}

Recently, we studied the equilibria of the potassium ion K^+ with benzene (25). The result given below shows that the bonding to potassium is much stronger than than to Cl^-. Calculations indicated that the most stable $K^+(C_6H_6)$ complex has an axial structure in which the K^+ lies on the symmetry axis of the benzene molecule. Benzene has a quadrupole moment of negative sign which is located on the symmetry axis in the centre of the molecule. The positive ion, when in the axial position, maximizes the attraction with the quadrupole and also achieves a substantial energy lowering due to the polarizability of the π electron rings. For Cl^-, the axial position leads to a repulsive interaction with the quadrupole moment, and bonding that is considerably weaker than that calculated for structure VI.

$$K^+ + C_6H_6 = K^+(C_6H_6) \qquad -\Delta H^0 \approx 18\ \text{kcal mol}^{-1}$$

Structures VIII–XIII (Fig. 6) illustrate the bonding of fluorobenzenes to Cl^{-1}. The hydrogen atom *meta* to the fluorine substituent has the largest net atomic positive charge (based on Mullikan population analysis, STO-3G basis set). The strongest hydrogen bond with Cl^- is obtained with that hydrogen. The stronger hydrogen bonding in the *meta* rather than *para* position to the fluorine substituent must be due to π donation from the fluorine. While σ withdrawal from the fluorine strengthens the hydrogen bond to Cl^-, π donation weakens it. The effect of π donation is smallest for the *meta* position. Increased fluorine substitution in the *meta* position in the series benzene, fluorobenzene, and 1,3-difluorobenzene can be expected to lead to increases of the chloride affinities. This in fact is observed experimentally (Table 2) and is also predicted by the calculations. The composite Fig. 7 shows that there is a linear relationship between the calculated and measured chloride binding energies and between the binding energies and the net atomic charge on the most positive hydrogen.

The chloride affinities of monosubstituted halobenzenes (see Table 2) increase in the order F, Cl, Br, I. The same order was found for the gas phase acidities of halosubstituted acetic acids (26). To explain the acidities of the acetic acids, the increased polarizability in the order F → I was invoked (26). In the present situation also, the increased polarizability should be the major effect, decreased π donation in the F → I order may be another contributing factor.

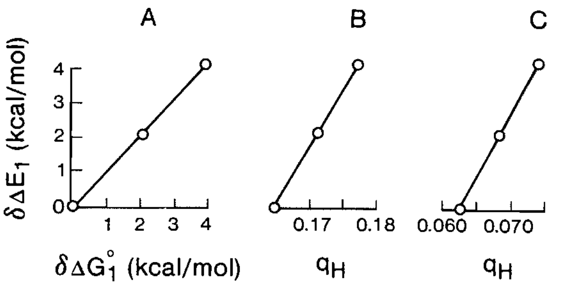


FIG. 7. Results for benzene, fluorobenzene, and difluorobenzene. Figure A shows STO-3G calculated ($\delta\Delta E_1$) versus measured ($\delta\Delta G_1^0$) energy of reaction: $FC_6H_5Cl^- + C_6H_6 = FC_6H_5 + C_6H_6{\cdot}Cl^-$. Figure B gives $\delta\Delta E$ versus net atomic positive charge on interacting hydrogen in complex $RHCl^-$. Figure C shows the same but for net positive charge on RH before formation of complex $RHCl^-$.

The first report of hydrogen bonding involving an aromatic C—H as hydrogen donor was made by Allerhand and Schleyer (27). It was based on observation of an infrared association band for 1,3,5-trichlorobenzene and pyridine in carbon tetrachloride solvent. A hydrogen bonded complex with 1,3-dichlorobenzene was not observed under the same conditions (27). Unfortunately we did not make measurements with 1,3,5-trifluorobenzene or 1,3,5-trichlorobenzene. However, from the trends observed for the halobenzenes that were measured and calculated above, one may conclude that the chloride affinities of 1,3,5-trifluoro- and 1,3,5-trichlorobenzene should be higher than those for the 1,3 disubstituted compounds. Therefore our results are in line with the findings of Allerhand and Schleyer. The fact that they did not observe the more weakly bonded dichloro complex must be attributed to solvent effects. More recently Benoit and co-workers (4) reported that they did not observe a complex between 1,3,5-trichlorobenzene and Cl^- in sulfolane solvent. Again this is obviously a solvent effect, the polar and abundant solvent displacing completely the trichlorobenzene from the Cl^- complex.

Structures XIV, XV, and XVI provide an insight into the bonding of Cl^- to toluene and by inference also for the substituted toluenes. In the lowest energy structure XIV, Cl^- hydrogen bonds to one of the aromatic hydrogens. However, the structure XV, in which Cl^- hydrogen bonds to one of the benzyl hydrogens, is less stable by only 0.4 kcal/mol. This suggests that, for the substituted toluenes with higher acidity than toluene, attachment of the Cl^- will occur to the most acidic hydrogen, i.e. to a benzylic hydrogen. To this extent, one can say that the present STO-3G calculations are supportive of the findings based on the experimental chloride affinities, where the correlation of the affinities with the gas phase acidities of the toluene was

Can. J. Chem. Downloaded from www.nrcresearchpress.com by CLEMSON UNIVERSITY on 11/13/14
For personal use only.

taken to imply that hydrogen bonding to the benzylic hydrogen occurs.

The results for structures XVII–XIX, dealing with Cl^- and acetone, throw some light on the bonding of Cl^- to carbon acids with carbonyl groups. The most stable structure is XVII where the Cl^- is hydrogen bonded to one of the acidic hydrogens of the methyl group. The bond in XVIII, where Cl^- is in line with the CO dipole is predicted to be of comparable but somewhat weaker strength. The correlation with the gas phase acidity observed for the carbonyl carbon acids in Fig. 5, i.e. progressively higher chloride affinities in the series Me_2CO, MeCOPh. $PhCH_2COMe$ and $(MeCO)_2CH_2$, taken together with the STO-3G prediction that the hydrogen bonded structure XVII is the most stable chloride, leads one to expect that, for the stronger acids also, the Cl^- hydrogen bonds to the most acidic hydrogen. For example for $(CH_3CO)_2CH_2$ the Cl^- attachment should be to one of the methylene hydrogens.

Acetone is another solvent molecule for which the bonding to the negative ion (Cl^-) $-\Delta H$ = 13.7 kcal mol^{-1}, is considerably weaker than that to the positive ion (K^+) of similar radius. Measurements from this laboratory (25) give a $-\Delta H$ = 24.4 kcal mol^{-1} for the potassium ion. The reason for this difference is easily understood. The bonding is largely of an electrostatic nature. Most of the permanent dipole is in the CO bond. The positive ion can approach the CO dipole closely. On the other hand, the negative ion is kept from close approach by the presence of the methyl groups.

A comparison between the calculated ΔE_1 (STO-3G) for the most stable structures and the measured ΔG_1° is shown in Fig. 8. One may expect that the ΔS_1° differences for the different RH are not very large. In such a case an approximately linear relationship between ΔE_1 and ΔG_1° should be observed. Such a relationship is indicated in Fig. 8, however, the data are quite scattered. This is probably due to the considerable difference in the nature of the compounds RH included in the figure.

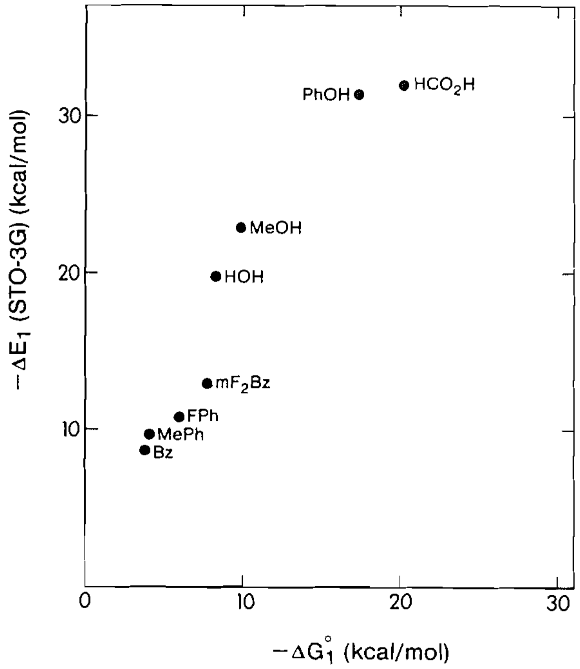


FIG. 8. Plot of calculated ΔE(STO-3G) for reaction [1] ($RH + Cl^- = RHCl^-$) versus measured ΔG_1° for same reaction. ΔG_1° values from Table 2.

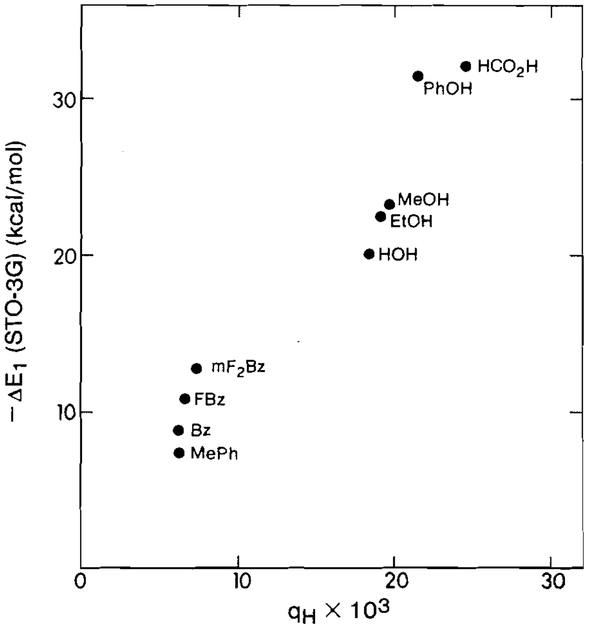


FIG. 9. Plot of ΔE(STO-3G) for reaction [1] versus net positive charge on acidic hydrogen of RH before the reaction.

In the preceding discussion it was noted that for related compounds there is a near linear relationship between the net atomic charge of the hydrogen in the RH and the hydrogen bond in the complex $RHCl^-$. This relationship is further explored in the data shown in Fig. 9, which contains the results for the substituted benzenes, the hydroxylic compounds, HOH, MeOH, EtOH, and phenol, and formic acid. It can be seen that the relationship does not hold up as well when strongly differing groups of compounds are included. Still, an approximate proportionality is observed, which suggests that the net atomic charges in the hydrogens of RH are a rough guide to the strength of the hydrogen bond with the negative ion. A much better relationship is observed when the hydrogen

Can. J. Chem. Downloaded from www.nrcresearchpress.com by CLEMSON UNIVERSITY on 11/13/14
For personal use only.

bond energies are plotted versus the charge on the chlorine in the complex $RHCl^-$. This is shown in Fig. 10. Since the charge in the separated Cl^- is -1, the figure shows that the strength of the hydrogen bond in $RHCl^-$ increases in proportion with the negative charge transferred from Cl^- to the molecule RH, on formation of the complex $RHCl^-$.

Benoit and co-workers (4) have determined the enthalpy change $\Delta H_{1(sl)}$ for reaction [1] occurring in sulfolane solution. These results are given in Table 1. Comparing the ΔH_1 for gas phase and solution, we notice that the exothermicity is much attenuated in solution. The attenuation factor is not constant but is in the range 7 for the stronger acids HCO_2H and phenol and 5 for the weaker HOH and CH_3OH. Benoit (4) has also determined the enthalpy of solvation of RH from gas phase to sulfolane (see Table 1) so that the cycle [2] can be set up, which leads to eqs. [3] and [4]. Equation [4] is of

$$\begin{tikzcd}
\mathrm{RH_{(g)} + Cl^-{}_{(g)}} \arrow[r, "\Delta H_{1(g)}"] & \mathrm{RHCl^-{}_{(g)}} \arrow[d, "\Delta H_{sl}(RHCl^-)"] \\
\mathrm{RH_{(sl)} + Cl^-{}_{(sl)}} \arrow[u, "\begin{matrix}-\Delta H_{sl}(RH)\\-\Delta H_{sl}(Cl^-)\end{matrix}"] \arrow[r, "\Delta H_{1(sl)}"] & \mathrm{RHCl^-{}_{(sl)}}
\end{tikzcd} \quad [2]$$

$$[3] \quad \Delta H_{1(sl)} = -\Delta H_{sl}(RH) - \Delta H_{sl}(Cl^-) + \Delta H_{1(g)} + \Delta H_{sl}(RHCl^-)$$

$$[4] \quad \Delta H_4 = \Delta H_{sl}(RHCl^-) - \Delta H_{sl}(Cl^-) = \Delta H_{1(sl)} - \Delta H_{1(g)} + \Delta H_{sl}(RH)$$

interest since it provides ΔH_4, the solvation energy difference between the complex $RHCl^-$ and Cl^-. These results are given in Table 1. ΔH_4 is always positive, as is to be expected. One might have also expected that ΔH_4 will increase with the size of the RH molecule, i.e. ΔH_4 should be larger for phenol than for formic acid. However this trend is not observed, ΔH_4 (phenol) = 7.7 kcal/mol while $\Delta H_4(HCO_2H)$ = 12.4 kcal/mol. The clear trend observed is that ΔH_4 increases with the acidity of RH. On reflection, the reason for this trend becomes clear. The solvation of $RHCl^-$ will decrease with the radius of RH only if substantial negative charge is delocalized onto RH. This delocalization depends on the extent of proton transfer from RH to Cl^-, i.e. on the acidity of RH. An even more direct measure is the STO-3G calculated charge transfer from Cl^- to RH. Figures 5 and 9 demonstrate the proportionality between the charge transfer from Cl^-, the chloride affinity of RH, and the acidity of RH. Evidently, ΔH_4 will depend on the extent of charge transfer from Cl^- to RH, the sites on RH to which the charge is transferred, i.e. extent of delocalization within RH and the size of RH. The operation of some of these combined effects should be reflected in the available ΔH_4. Unfortunately, these are very few and not of high accuracy. One case fits the expected trend. The extent of charge transfer in $ClHCl^-$ should be by far the largest, i.e. 0.5 electrons, since the two Cl atoms become equivalent, (for the other $\delta q Cl^-$, see Table 3). The observed ΔH_4 for HCl is large but not by far the largest. This must be due to the small size of HCl, i.e. even though the charge transfer is large, the overall size of the ion $ClHCl^-$ is small, and this reduces the adverse effect on the solvation energy of the ion.

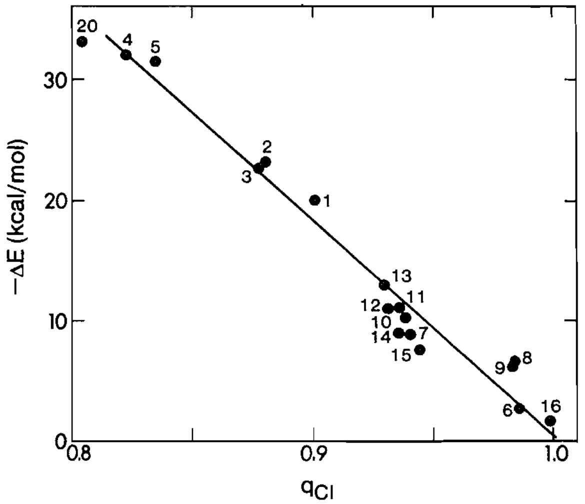


FIG. 10. Plot of ΔE(STO-3G) from reaction [1] versus net negative charge on Cl^- in $RHCl^-$. Numbers on data points correspond to structures (in roman numerals) in Fig. 7. Plot shows good correlation between the bonding in the complex $RHCl^-$ and the charge transferred from Cl^- to RH on formation of the complex $RHCl^-$.

The attenuation of the observed hydrogen bonding in solution relative to the gas phase is closely analogous to the attenuation of substituent effects on acidity or basicity in the gas phase and solution. For example, a substituent which increases the gas phase acidity of benzoic acid delocalizes the charge in the benzoate anion and reduces the solvation energy of the substituted anion. This leads to an attenuation of the substituent effect in solution (21). In the hydrogen bonding complexes the role of the substituent is played by HR. An HR that forms a strong hydrogen bond, i.e. stabilizes Cl^- strongly, decreases the solvation energy of $RHCl^-$ strongly and this leads to an attenuation of the hydrogen bonding in solution.

The gas phase hydrogen bonding energies could be useful in the design of multiligand complexing agents, i.e. crypts (5) for negative ions. Data from solutions often do not express the true available complexing power of a complexing group in a crypt. For example, the enthalpy changes $\Delta H_{1(l)}$ for

Can. J. Chem. Downloaded from www.nrcresearchpress.com by CLEMSON UNIVERSITY on 11/13/14
For personal use only.

CH_3OH and CH_3CO_2H in sulfolane are equal, $\Delta H_{1(l)} = -3.2$ kcal/mol (4). Yet it is clear from the gas phase data that a carboxylic acid or a phenolic hydroxide group is vastly superior to the OH group from an aliphatic alcohol. Since the radius of the crypt as a whole is dictated largely by other considerations, it is clear that a great advantage in complexing is to be gained by selecting the most acidic hydroxide groups as ligands on the inside of the crypt.

The data in Table 2 give the order of stabilities of $RHCl^-$ gas phase complexes. Thus they have direct application to negative ion chemical ionization mass spectrometry of Cl^- adducts (2). It is clear that adducts of a wide variety of compounds can be formed and that considerable selectivity can be obtained if the ion source temperature is varied from room temperature to 300°C. At room temperature, or below, adducts with all compounds in Table 2 will be formed. At the highest temperatures only adducts with the strongest acids will be observable.

1. J. L. Puckett and W. C. Lineberger. Phys. Rev. A, **1**, 1635 (1970); F. C. Fehsenfeld, C. J. Howard, and A. L. Schmellekpf. J. Chem. Phys. **63**, 2835 (1975); J. A. Davidson, F. C. Fehsenfeld, and C. J. Howard. Int. J. Chem. Kinet. **9**, 17 (1977).
2. H. P. Tannenbaum, J. D. Roberts and R. C. Doherty. Anal. Chem. **47**, 49 (1975).
3. J. E. Gordon. J. Org. Chem. **26**, 738 (1961); I. M. Kolthoff and M. K. Chantooni, Jr. J. Am. Chem. Soc. **91**, 4621 (1969).
4. S. Y. Lam, C. Louis, and R. L. Benoit. J. Am. Chem. Soc. **98**, 1156 (1976).
5. J. M. Lehn. Pure Appl. Chem. **50**, 871 (1978).
6. R. A. Durst (*Editor*) Ion selective electrodes. NBS Special Publications 341. U. S. Government Printing Office, Washington, D. C. 1969.
7. R. Yamdagni and P. Kebarle. J. Am. Chem. Soc. **93**, 7139 (1971).
8. (*a*) R. Yamdagni, J. D. Payzant, and P. Kebarle. Can. J. Chem. **51**, 2507 (1973); (*b*) M. Arshadi, R. Yamdagni, and P. Kebarle. J. Phys. Chem. **74**, 1475 (1970); (*c*) P. Kebarle. Annu. Rev. Phys. Chem. **28**, 445 (1977).
9. M. A. French, J. Cumming, and P. Kebarle. J. Am. Chem. Soc. **99**, 6999 (1977).
10. J. B. Cumming and P. Kebarle. Can. J. Chem. **56**, 1 (1978).
11. J. E. Bartmess, J. A. Scott, and R. T. McIver, Jr. J. Am. Chem. Soc. **101**, 6045 (1979).
12. J. Sunner and P. Kebarle. J. Phys. Chem. **85**, 327 (1981).
13. Y. K. Lau, S. Ikuta, and P. Kebarle. J. Am. Chem. Soc. **104**, 1062 (1982).
14. W. J. Hehre, R. F. Stewart, and J. A. Pople. J. Chem. Phys. **51**, 2657 (1969); J. A. Pople and M. Gordon. J. Am. Chem. Soc. **89**, 4293 (1967); Gaussian 70: W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople. QCPE, **11**, 236 (1973); Hondo 5: M. King, M. Dupuis, and J. Rys. Nat. Resour. Comput. Chem. Software Cat. Vol. 1. Prog. No. QH02, Hondo 5 (1980).
15. (*a*) M. D. Harmony, V. W. Laurie, R. L. Kuczkowski, R. H. Schwedeman, D. A. Ramsay, F. J. Loras, M. J. Lafferty, and A. G. Maki. J. Phys. Chem. Ref. Data, **8**, 619 (1979); (*b*) J. E. DelBene, F. T. Marchese, G. T. Worth, and M. E. Conrad. Theoret. Chim. Acta, **36**, 195 (1975).
16. (*a*) E. Clementi, H. Clementi, and D. R. Davis. J. Chem. Phys. **46**, 4725 (1967); (*b*) E. Clementi, J. Mehl, and W. von Niessen. J. Chem. Phys. **59**, 508 (1971).
17. R. Yamdagni and P. Kebarle. Can. J. Chem. **52**, 2449 (1974).
18. W. R. Davidson, J. Sunner, and P. Kebarle. J. Am. Chem. Soc. **101**, 1675 (1979).
19. W. F. Reynolds, P. G. Mezey, W. J. Hehre, R. D. Topsom, and R. H. Taft. J. Am. Chem. Soc. **99**, 5821 (1977).
20. W. J. Hehre, M. Taagepera, R. W. Taft, and R. D. Topsom. J. Am. Chem. Soc. **103**, 1344 (1981).
21. T. B. McMahon and P. Kebarle. J. Am. Chem. Soc. **99**, 2222 (1977).
22. M. Fujio, R. T. McIver, and R. W. Taft. J. Am. Chem. Soc. **103**, 4017 (1981)
23. H. Kistenmacher, H. Popkie, and E. Clementi. J. Chem. Phys. **59**, 5842 (1973).
24. P. Kollman and I. Kuntz. J. Am. Chem. Soc. **98**, 6820 (1976).
25. J. Sunner, K. Nishizawa, and P. Kebarle. J. Phys. Chem. **85**, 1814 (1981).
26. K. Hiraoka, R. Yamdagni, and P. Kebarle. J. Am. Chem. Soc. **95**, 6833 (1973).
27. A. Allerhand and P. v R. Schleyer. J. Am. Chem. Soc. **85**, 1715 (1963).