Pyrolysis of ^{13}C-Enriched Phenyltrimethylsilyldiazomethane. ^{13}C-Enriched phenyltrimethylsilyldiazomethane was injected into a gas chromatograph under condition B. The product, ^{13}C-enriched 1,1-dimethyl-1-silabenzocyclopentene, was isolated in a cold trap at −78 °C: NMR (CCl_4) δ 0.31 (6 H, s), 1.00 (2 H, t), 3.02 (2 H, t), 6.95–7.51 (4 H, m); mass spectrum (70 eV) *m/e* (measured intensity) 163 (13.2), 162 (32.5), 120 (2.1), 119 (5.5); mass spectrum *m/e* 119.0318 ± 0.0006 (calcd for C_7H_7Si, *m/e* 119.0317); ^{13}C NMR from Me_4Si (intensity) 153.11 (124 992), 139.86 (1 183 552), 131.93 (495 616), 129.20 (608 256), 125.56 (1 042 816), 31.80 (288 640), 11.47 (177 600), −1.59 (230 336).

Pyrolysis of ^{13}C-Enriched Phenyl Trimethylsilyl Ketone Tosylhydrazone Salt. Enriched (12.8% ^{13}C) salt was flash-pyrolyzed by method C to produce, after isolation by gas chromatography under condition B, enriched (13.0% ^{13}C) **6**.

References and Notes

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(2) (a) Portions of this work were communicated previously[3,4] and others are taken from the Ph.D. Theses of R.R.G. (Princeton, 1976) and J.A.K. (Iowa State, 1976) and the A.B. Thesis of A.J.R. (Princeton, 1975). (b) The University of Tsukuba. (c) Princeton University. (d) Iowa State University.

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Effects of Charge Delocalization on Hydrogen Bonding to Negative Ions and Solvation of Negative Ions. Substituted Phenols and Phenoxide Anions

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Abstract: Measurements of gas phase ion equilibria with a pulsed electron beam high ion source pressure mass spectrometer lead to the $\Delta G°$ and $\Delta H°$ values for the reactions $AHCl^- = AH + Cl^-$ and $AHCl^- = A^- + HCl$, where AH stands for substituted phenols. These results show that the hydrogen bond energies in $AHCl^-$ (for dissociation to $Cl^- + HA$) increase linearly with the gas phase acidity of the phenols. The hydrogen bond energies for dissociation of $AHCl^-$ to $A^- + HCl$ increase linearly with increase of the (gas phase) basicity of the phenoxide ions A^-. Comparison with investigations of the $AHCl^-$ complexes in acetonitrile by Kolthoff and Chantooni shows that the substituent effects in acetonitrile are strongly attenuated. It is suggested that in acetonitrile the extent of proton transfer on formation of $AHCl^-$ from AH and Cl^- is much smaller than that occurring in the gas phase. Proton transfer leads to charge dispersal in $AHCl^-$ which would decrease the solvation of $AHCl^-$. The decrease of hydrogen bonding in A^-–HCl with decreasing basicity of A^-, i.e., increasing acidity of AH, is related to an expected decrease of hydrogen bonding in A^-–$(HOH)_n$ which is responsible for the attenuation of the acidities of phenols in aqueous solution.

Earlier studies of the gas phase equilibrium

$$BHR^- = B^- + HR \qquad (1)$$

executed in this laboratory[1-5] showed that the strength of the hydrogen bond (i.e., $\Delta H_1°$ and $\Delta G_1°$) increased with the (gas phase) acidity of HR and the basicity of B^-. For example, study of the series[3] where $B^- = Cl^-$ and HR = HOH, CH_3OH, $(CH_3)_3COH$, Cl_3CH, C_6H_5OH, CH_3COOH, HCOOH gave $\Delta H_1°$ and $\Delta G_1°$, values which were found to increase in the order shown above, which is also the order of increasing gas phase acidity.[6] In another series[4] where HR = H_2O was kept constant and B^- was changed, it was found that the hydrogen bond strengths increased almost linearly with the basicity of $B^- = I^-, Br^-, NO_3^-, Cl^-, NO_2^-, F^-, OH^-$.

Results involving positive ions B_1H^+ like H_3O^+, $CH_3OH_2^+$, $(CH_3)_2OH^+$, NH_4^+, $CH_3NH_3^+$, etc., and molecules B_2 like H_2O, CH_3OH, $(CH_3)_2O$, NH_3, CH_3NH_2, etc., also showed[7-10] that the strength of the hydrogen bond in $B_1HB_2^+$ increases with the acidity of B_1H^+ and the basicity of B_2.

The existence of homoconjugated (AHA^-) and heteroconjugated (BHA^-) complexes in solution has been long known. These complexes are particularly stable in aprotic solvents and have been subjected to numerous studies[11] in these media. On the whole, considerable parallels exist regarding stabilities of the complexes in the gas phase[1-5] and in aprotic solvents. Thus, Gordon[12] found that the stabilities of the complexes AHA^- (log *K* values in acetonitrile, AH benzoic acids) increased linearly with the aqueous acidities of the acids

AH. Other studies[11,13,14] have shown that the stability of B^-HA generally increases with the basicity of B^- and the acidity of HA. However, the results in aprotic solutions are considerably more complex than those in the gas phase. This is caused by specific solvent differences and ion pairing, i.e., dependence on the nature of the cation used. Furthermore since the acidity orders of the proton donors AH may be reversed in different solvents, a clear correlation between acidity of AH and stability of B^--HA can often not be established. The same holds true for the relationship with the basicity of the proton acceptor B^-.

The systems studied in the present work involve the interactions of Cl^- with HA where HA stands for substituted phenols. The acidities in substituted phenols in the gas phase were recently determined in this laboratory.[15] Furthermore the acidity order of substituted phenols in the gas phase, aqueous solution, and the aprotic solvent dimethyl sulfoxide is essentially the same[15,16] so that a good comparison can be made between the gas phase results for the complexes Cl^-HA and recent quantitative results for the same system in acetonitrile.[17]

As was pointed out earlier,[15,18] results on the stability of complexes B^--HA are of interest not only from the standpoint of hydrogen bonding interactions. They also have a bearing on ionic solvation by protic solvents. As an example we can consider the solvation of substituted phenoxide anions. The recent measurement of the gas phase acidities of substituted phenols[15] allowed a detailed comparison of the gas phase and aqueous acidities to be made. It was found[15] that a linear relationship between gas phase and aqueous acidities of the phenols existed. However, the substituent effects in aqueous solution were attenuated by a factor of seven. Evidently a linear relationship with such a large attenuation can result only if there is a proportional relationship between the intrinsic, electronic effect of the substituent and an opposing solvation effect caused by the same substituent. It has been long recognized that the unfavorable solvation effect of an acidifying substituent lies mostly in the reduction of the solvation energy of the substituted anion. For the present case, a Born cycle analysis involving the gas phase and aqueous acidities of phenols done by Arnett[19] has shown that a substituent that increases the gas phase acidity decreases the solvation energy of the substituted phenoxide ion by a similar amount. It is natural to connect this cancellation effect with the hydrogen bonding interactions discussed above. A substituent that increases the acidity of BH decreases the basicity of the conjugate base B^-. Therefore the hydrogen bond with the first *and subsequent*[20] protic solvent molecules RH will be weaker. This means the solvation energy of B^- will be lower. This decrease of hydrogen bonding energies between B^- and $(HR)_n$ with increase of acidity of BH must be providing the automatic mechanism for the large attenuation of the substituent effect. Results on bonding between PhO^- HCl obtained in the present work allow a further exploration of this relationship.

Experimental Section

The measurements of the ion-molecule equilibria were made with a pulsed electron beam high ion source pressure mass spectrometer which has been described earlier.[21] Briefly, the principle of the measurement is as follows. A suitable gas mixture containing methane as buffer gas (1-4 Torr), ~3 mTorr CCl_4, and accurately known pressures of the phenols AH in the 5-20 mTorr range was passed in slow flow in and out of the temperature-controlled ionization chamber. Ionization was obtained by a short (microseconds) pulse of electrons. The dissociative electron capture: $e + CCl_4 = Cl^- + CCl_3$, produces chloride ions which react with the phenols AH by the association reaction 2.

$$Cl^- + AH = AHCl^- \quad (2)$$

When more than one phenol is present also the exchange reaction 3 occurs.

$$A_xHCl^- + A_yH = A_xH + A_yHCl^- \quad (3)$$

Most of the ions diffuse to the walls of the ionization chamber where they become discharged. Some of the ions come to the vicinity of the ion exit slit through which they escape into an evacuated region where they are accelerated by electric fields, magnetically separated according to mass and detected with an ion-counting multiscaler system. The ion intensities can be observed for some 10 ms after the electron pulse. For the stated concentration conditions, the initial, kinetic stage in which the relative ion concentrations change, is short ($<100\ \mu s$). After this stage, the relative ion concentrations become constant, which generally means that equilibrium has been achieved.

In principle, the required data could be obtained by measuring in separate experiments the association equilibria 2 using one phenol at a time. However, since the differences: $\Delta\Delta H_2°$ and $\Delta\Delta G_2°$, when differently substituted phenols are used, are small compared with the $\Delta H_2°$ and $\Delta G_2°$ values, it is advantageous to measure the exchange equilibria 3 involving different phenols and obtain in this manner the relative values directly. Absolute values $\Delta H_2°$ and $\Delta G_2°$ can then be obtained by measuring the equilibrium 2 and corresponding $\Delta G_2°$ and $\Delta H_2°$ with one given phenol, most suitably the unsubstituted phenol, and then combining this result with the relative results from the exchange equilibria 3. This approach has also the advantage that multiple cycles can be applied to reaction 3 (see Results). What's more important, by this approach a significant source of error occurring for reaction 2 can be much reduced. When clustering equilibria like 2 are measured; the results are generally somewhat affected by a partial dissociation of the ions $AHCl^-$ to Cl^- and AH in the region immediately outside the ion exit slit.[22] This nonequilibrium creation of Cl^- ions has a bigger effect on K in the low temperature region, where K, i.e., $[AHCl^-]/[Cl^-]$, is large, since in this case a small nonequilibrium increase of Cl^- causes a big decrease in the ion ratio.[22] In practice this effect restricts the available temperature range in the van't Hoff plots of K_2. Since Cl^- is not measured in 3, meaningful measurements of K_3 can be obtained also in the region where $[AHCl^-]/[Cl^-]$ is large. This improves the accuracy of the relative values for the different phenols.

Since CN phenol is a stronger gas phase acid than HCl,[15] the equilibria 3 involving this phenol could be measured only after addition of HCl to the gas mixture. This shifted the equilibrium $CN\text{-}PhOH + Cl^- = CN\text{-}PhO^- + HCl$ to the left. In the absence of HCl the dominant association was not $CN\text{-}PhOHCl^-$ but the proton-held dimer $(CN\text{-}PhO)_2H^-$.

Results

The van't Hoff plots for the measured exchange equilibrium

$$A_xHCl^- + A_yH = A_xH + A_yHCl^- \quad (3)$$

where A_xH and A_yH are two differently substituted phenols, are shown in Figure 1. The $\Delta G_3°$ and $\Delta H_3°$ obtained from these plots can be combined, as shown in Figure 2, to obtain $\Delta G_4°$ and $\Delta H_4°$ for reaction 4 which measures the difference for the hydrogen bond dissociation energies between the substituted phenols HA and phenol HA_0.

$$AHCl^- + A_0H = AH + A_0HCl^- \quad (4)$$

$$\Delta H_4 = D(AH\text{-}Cl^-) - D(A_0H\text{-}Cl^-)$$

The multiple cycles in Figure 2 are not entirely consistent. This gives an indication on the magnitude of the errors in the measurement. The biggest discrepancy is the difference between phenol and chlorophenol which when measured directly gives $\Delta H_4 = 3.9$ kcal/mol, while the two step measurement via fluorophenol gives only 2.7 kcal/mol. The agreement in the other multiple cycles is better so that an error of ~20% is indicated for the $\Delta G_4°$ and $\Delta H_4°$ given in Figure 2.

Evidently the accuracy of the measurement of the equilibria 3 is lower than that obtained in measurements of proton transfer equilibria. For these reactions, the $\Delta G°$ values, obtained at a single temperature, when displayed in multiple

Table I. Thermochemical Data[a] from Gas Phase Ion Equilibria

HA[b]	ΔH_4,[c] D(Cl-HA) $- D$(Cl$^-$-HA$_0$)	ΔH_5,[d] D(A$_0^-$-HCl) $- D$(A$^-$-HCl)	ΔH_6,[e] D(A$_0^-$-H$^+$) $- D$(A$^-$-H$^+$)	D(Cl$^-$-HA)[f]	D(A$^-$-HCl)[g]	D(A$^-$-H$^+$)[e]
Me	− 0.4	− 0.9	− 1.3	24.1	40	349.5
H	0	0	0	24.5	39.1	348.2
F	1.9	0.7	2.6	26.4	38.4	345.6
Cl	3.6	3.0	6.6	28.1	36.1	341.6
CN	9.1	8.6	17.7	33.6	30.5	330.5
HCl	−	−	−	24	−	333.6

[a] All values in kilocalories/mole; HA, substituted phenols; HA$_0$, phenol. [b] Groups shown in this column correspond to para substituents of phenol, except HCl which corresponds to hydrochloric acid. [c] ΔH_4, from van't Hoff plots in Figure 1 and cycles in Figure 2. [d] ΔH_5 obtained from ΔH_4 and ΔH_6 using eq 8: $\Delta H_4 + \Delta H_5 = \Delta H_6$. [3] Gas phase acidities from ref 6 and 15. [f] Calculated from D(Cl$^-$-HOC$_6$H$_5$) = 24.5 + 3 kcal/mol.[23] [g] Calculated from eq 10; see text.

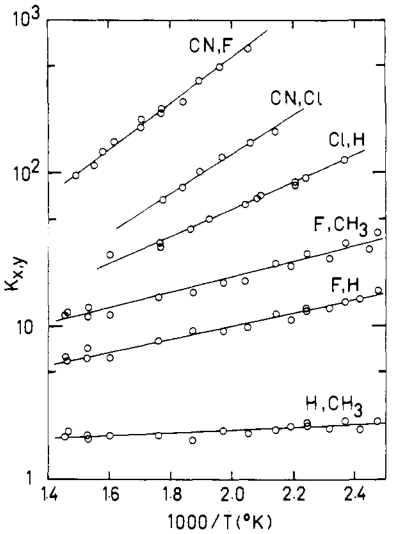


Figure 1. van't Hoff plots for equilibria 3: A$_x$HCl$^-$ + A$_y$H = A$_x$H + A$_y$HCl$^-$, where A$_x$H and A$_y$H are para monosubstituted phenols. Substituents x and y given over each plot.

cycles are generally consistent to 0.1-0.3 kcal/mol (see, for example, ref 15). The larger error in the determination of equilibria 3 is probably due to the different temperatures used and the already mentioned collision-induced dissociation of Cl$^-$HA outside the ion source (see Experimental Section).

The differences of hydrogen bond energies for bonding of HCl to differently substituted phenoxide anions can be obtained from eq 5.

$$\mathrm{A^- + A_0HCl^- = AHCl^- + A_0^-} \tag{5}$$

$$\Delta H_5 = D(\mathrm{A_0^-\text{-}HCl}) - D(\mathrm{A^-\text{-}HCl})$$

The known relative gas phase acidities of the phenols,[11] shown in reaction 6, can be used in conjunction with the thermodynamic cycle 7 to evaluate the ΔH_5 values:

$$\mathrm{A_0H + A^- = A_0^- + AH} \tag{6}$$

$$\Delta H_6{}^\circ = D(\mathrm{A_0^-\text{-}H^+}) - D(\mathrm{A^-\text{-}H^+})$$

$$\begin{tikzcd}
\mathrm{A_0HCl^- + A^- + H^+} \arrow[r, "\Delta H_5"] & \mathrm{A_0^- + AHCl^- + H^+} \arrow[d, "\Delta H_b"] \\
\mathrm{A_0HCl^- + AH} \arrow[u, "\Delta H_a"] & \mathrm{A_0H + AHCl^-} \arrow[l, "\Delta H_4"']
\end{tikzcd} \tag{7}$$

From $\Delta H_4 + \Delta H_a + \Delta H_5 + \Delta H_b = 0$ and $\Delta H_a + \Delta H_b = -\Delta H_6$, one obtains eq 8.

$$\Delta H_6 = \Delta H_4 + \Delta H_5 \tag{8}$$

Since ΔH_4 and ΔH_6 are available, ΔH_5 can be calculated. The values for ΔH_4, ΔH_5, and ΔH_6 are summarized in Table I.

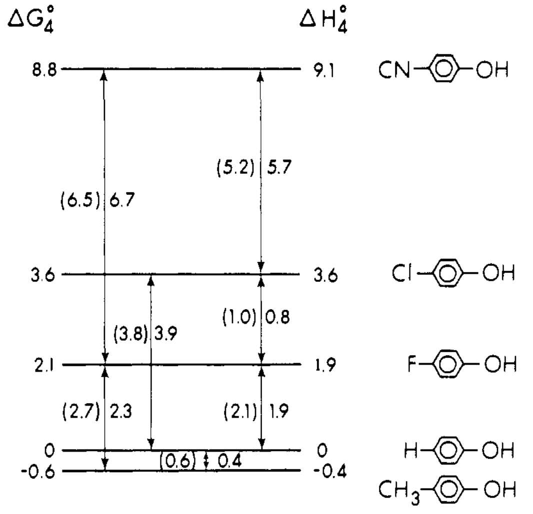


Figure 2. Summary of enthalpy and free energy changes for reactions 3: A$_x$HCl$^-$ + A$_y$H = A$_x$H + A$_y$HCl$^-$ obtained from van't Hoff plots in Figure 1. $\Delta H_3{}^\circ$ given on left side of double arrows connecting A$_x$ and A$_y$. $\Delta G_3{}^\circ$ (at 300 K) given in parentheses on right side of double arrow. Columns $\Delta G_4{}^\circ$ and $\Delta H_4{}^\circ$ correspond to values for reaction 4: AHCl$^-$ + A$_0$H = AH + A$_0$HCl$^-$.

Table I gives also the absolute values D(AH-Cl$^-$) for the phenols. These data were obtained by substituting $\Delta H_9 = D(\mathrm{A_0H\text{-}Cl^-}) = 24.5$ kcal/mol into $\Delta H_4 = D(\mathrm{AH\text{-}Cl^-}) - D(\mathrm{A_0H\text{-}Cl^-})$. ΔH_9 was obtained by measurement[23] of the temperature dependence of the equilibrium.

$$\mathrm{A_0HCl^- = A_0H + Cl^-} \tag{9}$$

Also given in Table I are the absolute values D(A$^-$-HCl) which can be calculated from the cycle 10 since D(AH-Cl$^-$) and D(A$^-$-H$^+$) − D(Cl$^-$-H$^+$) are known (see Table I).

$$\begin{tikzcd}
 & \mathrm{AH + Cl^-} \arrow[dr, "D(\mathrm{A^-\text{-}H^+}) - D(\mathrm{Cl^-\text{-}H^+})"] & \\
\mathrm{AHCl^-} \arrow[ur, "D(\mathrm{AH\text{-}Cl^-})"] \arrow[rr, "D(\mathrm{A^-\text{-}HCl})"'] & & \mathrm{A^- + HCl}
\end{tikzcd} \tag{10}$$

Discussion

The results obtained are summarized in Table I and Figure 3. The plot on the left of Figure 3 gives D(Cl$^-$-HA) − D(Cl$^-$-HA$_0$) vs. D(A$_0^-$-H$^+$) − D(A$^-$-H$^+$) which corresponds to the change of the hydrogen bond energies Cl$^-$-HA with change of acidity of the phenols. The plot is seen to be approximately linear which demonstrates that the bond energy Cl$^-$-HA increases near linearly with increase of the phenol acidity.

The plot on the right of Figure 3 gives the hydrogen bond energy A$^-$-HCl vs. the changing acidity of AH, i.e., basicity

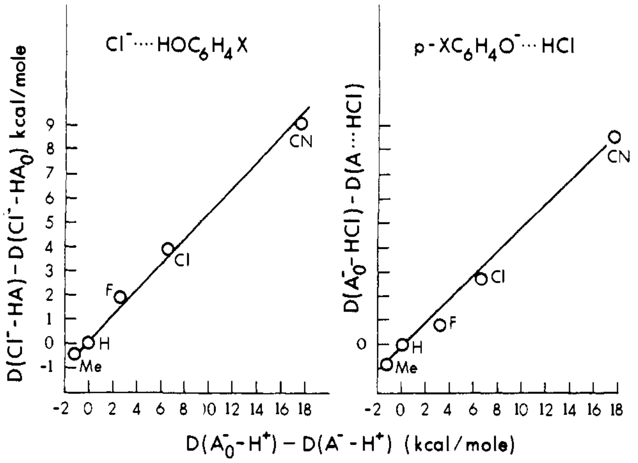


Figure 3. Left: plot of relative hydrogen bond energies in Cl^--HA vs. relative gas phase acidities of phenols HA; plot shows that hydrogen bond energy increases linearly with acidity of HA. Right: plot of relative hydrogen bond energies in A^--HCl vs. relative basicities of phenoxide ions A^-; results show that relative hydrogen bond energies increase linearly with relative (gas phase) basicity of phenoxide ions A^-; HA_0 is phenol and A_0^- is the unsubstituted phenoxide ion.

of A^-. The plot shows that the bond strength increases nearly linearly with increasing basicity of A^-.

It should be noted that the linear plot on the right of Figure 3 is a necessary consequence of the linear plot on the left. This follows from eq 8. Thus since ΔH_4 is proportional to ΔH_6, eq 8 requires that ΔH_5 is also proportional to ΔH_6. This is expressed in eq 11 where c is a proportionality constant.

$$\begin{aligned} \Delta H_4 &= c\Delta H_6 \\ \Delta H_5 &= (1 - c)\Delta H_6 \end{aligned} \qquad (11)$$

The value of c is equal to the slope of the left-hand plot in Figure 3, while the slope in the right-hand plot is equal to $1 - c$. Since in the present case $c \simeq 0.5$, $1 - c$ is also $\simeq 0.5$. The value of c must be related to the extent of proton transfer from AH to Cl^- occurring on formation of $AHCl^-$. A large value of c, i.e., c approaching unity, may be expected if complete proton transfer occurred and the interaction between the resulting A^- and HCl was quite similar for all A^-. On the other hand a a value of c much smaller than 0.5 would indicate that there is very little proton sharing. The present value of 0.5, therefore, does indicate a considerable proton sharing, a result which is consistent with the nearly equal gas phase acidity of the phenols and HCl. In fact CN-phenol is a stronger gas phase acid than HCl (see Table I).

The slope, c, observed on the left in Figure 3 appears constant only because the range of acidities of the phenols is relatively small. When compounds of lower and higher acidities are included in plots of Cl^--HA energy vs. acidity of HA, one obtains[24] curves in which the slope c increases with the acidity of HA.

Kolthoff and Chantooni[17] have measured the equilibria 12 involving the phenols AH in acetonitrile (AN).

$$(ClHA)^-_{AN} = (Cl^-)_{AN} + (HA)_{AN} \qquad (12)$$

They found that the hydrogen bond energies ($\Delta G_{12}°$) were linearly related to the aqueous acidities of the phenols. As mentioned earlier the aqueous and gas phase acidities of the phenols are also approximately linearly related.[15] Thus, the stability of $(ClHA)^-$ in the gas phase and in acetonitrile increases linearly with the acidity of the phenols.

Kolthoff and Chantooni plotted[17] the logarithm of the equilibrium constants for complex formation (the reverse of 12) vs. the Hammett σ values.[25,26] Such a Hammett-type plot is shown in Figure 4. Included in the figure are also the results from the present gas phase measurements of the reaction 4. The acetonitrile solvent data give, as was reported,[17] a good straight line. Significantly, a good fit of the p-NO_2 and 4-NO_2, 3Cl phenol was obtained by using the σ and not the σ^- substituent constants. It will be recalled[26] that π-electron-withdrawing substituents like CN and NO_2 can stabilize the phenoxide anion by conjugation across the ring as shown in structures I. In benzoate anions, the across-the-ring conjugation I is not important. Therefore the σ constants, which are obtained from the benzoic acids, do not give a good fit in linear free-energy plots involving compounds for which conjugation I is important. On the other hand the σ^- constants obtained from the aqueous acidities of the phenols do contain the effect of the conjugation I. Therefore Kolthoff and Chantooni[18] interpreted the fit to σ and not σ^- to mean that the resonance of type I is not important in the $ClHA^-$ complex and that this indicates that proton transfer from AH to Cl^- in $ClHA^-$ occurs to only a small extent.

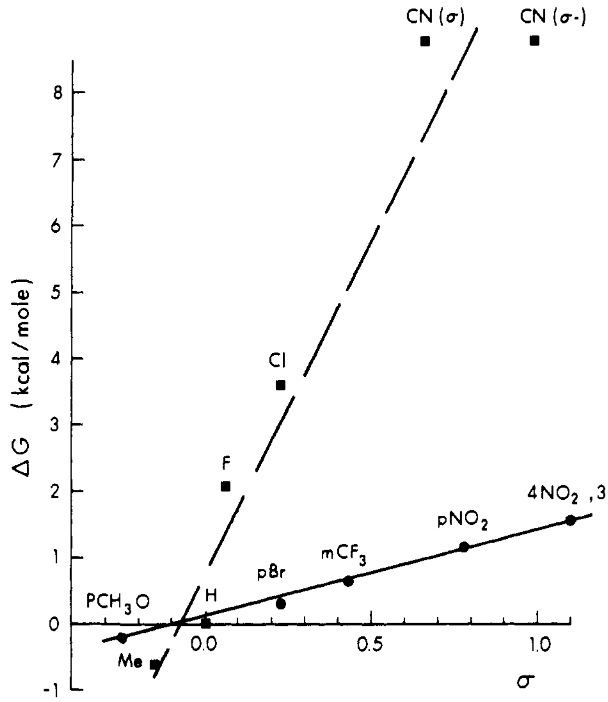
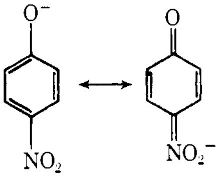


Figure 4. Comparison of hydrogen bonding in $AHCl^-$ in the gas phase and in acetonitrile. AH stands for substituted phenols and A_0H is phenol. $\Delta G°$ values correspond to free-energy change for reaction: $AHCl^- + A_0H = AH + A_0HCl^-$ at 300 K in the gas phase (present work) and in acetonitrile (Kolthoff and Chantooni[17]). σ values are for Hammett substituent constants.[19] Results show that substituent effect in acetonitrile is attenuated by a factor of about six relative to the gas phase (■, para substituents in the gas phase; ●, substituents in acetonitrile[17]).



I

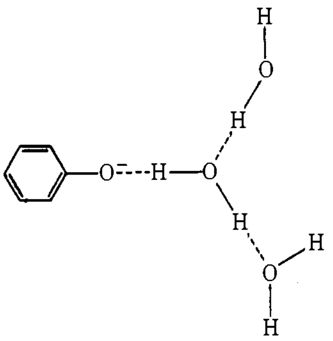
Unfortunately not quite enough experimental points from the gas phase measurements are available to define well the gas phase plot in Figure 4. The gas phase results obviously do not give as good a correlation with the σ values as the acetonitrile results. Therefore it is not possible to decide whether σ or σ^- gives a better fit for CN phenol.

It is interesting to note that the ratio of the slopes of the gas phase and acetonitrile results is ~6, which means that the substituent effect in acetonitrile is attenuated by this large factor. The attenuation of the substituent effect on the *acidity* of the phenols from gas phase to water was found[15] to be ~7. On the other hand the phenol acidities in Me_2SO were attenuated[15,16] only by a factor of <2. Since acetonitrile should be similar to Me_2SO, the large attenuation observed for the present process may appear surprising. However the formation of $AHCl^-$ from Cl^- and AH is a rather different process than the acid dissociation of AH. As was already pointed out, considerable proton transfer occurs in the gas phase on formation of the $AHCl^-$ complex. On the other hand Kolthoff and Chantooni's[17] results are consistent with a small extent of proton transfer in acetonitrile. Since the proton transfer in the solvent is very incomplete, the attenuation of the substituent effect for the $AHCl^-$ complex formation may be much larger than the (expected) small attenuation of the acidity of AH in acetonitrile which corresponds to total proton transfer to the solvent. The much smaller extent of proton transfer in acetonitrile may be understood on the following grounds. Proton transfer in $ClHA^-$ corresponds to electron transfer from Cl^- to A. This results in dispersal of ionic charge from the small Cl^- into the bulky phenyl group with attendant very large increase of the effective ionic radius and thus a large decrease of solvation.

One can expect that the attenuation of the substituent effect for $AHCl^-$ in protic solvents will be very much larger than that observed in the aprotic acetonitrile. As pointed out elsewhere,[15,24] charge dispersal in the negative ion and increase of (effective) negative ion radius have much less adverse effect on the solvation of the ion in aprotic solvents as compared to hydrogen bonding solvents.[27] Therefore much less proton transfer will occur in the $ClHA^-$ complex in protic solvents. In fact the bonding in such solvents is so weak that these complexes can not be observed in protic solvents under normal conditions.

We may turn now to Figure 3 (right) which shows that the binding energy in $ClHA^-$ for dissociation to A^- + HCl increases with the basicity of A^-. It is interesting to note that Kolthoff and Chantooni[17] also found a linear relationship between the basicities of the substituted phenoxide ions A^- and the hydrogen bond energy in $RH\text{-}A^-$ where RH was *p*-Br phenol. This is a relationship similar to that shown on the right-side of Figure 3 but with *p*-Br phenol rather than with HCl. In fact in the present gas phase measurements we often observed the presence of the proton-held phenol dimers ($A_xHA_y^-$). Their relative intensities did qualitatively agree with the expectation that the stability of $A_xHA_y^-$ relative to A_x^- and HA_y increases with the basicity of A_x^- and the acidity of HA_y. However, no quantitative measurements were made.

As was mentioned in the introduction, the decrease of the hydrogen bond energy in $A^-\text{-}HR$ with decrease of the basicity of A^-, i.e., increase of the acidity of AH, may be called upon to explain the linear relationship between the gas phase and the (attenuated) aqueous acidity of substituted phenols. It was suggested that the solvation of A^- is mostly due to hydrogen bonding of water molecules to the phenoxy group (see structure II) and that the hydrogen bond energies of the first several strongly interacting water molecules decrease with the decrease of the basicity of A^-, i.e., with increasing acidity of AH. The results shown in Figure 3 (right) are in line with the above argument. Of course for that purpose experimental gas phase measurements of the bonding in A^-HOH and $A^-(HOH)_n$ would have been much more pertinent than the A^-HCl results. The situation in A^-HOH is quite different from that for A^-HCl since HOH is a vastly weaker acid. Effectively very little proton transfer to A^- will occur on formation of A^-HOH. However, as mentioned earlier, a linear relationship between the basicities of NO_2^-, NO_3^-, CN^-, and the hydrogen bonding in these ions with HOH was found[9] and these cases also involve little proton transfer from HOH.



II

Attempts to measure the $A^-(HOH)_n$ equilibria in the presence of AH were unsuccessful since the much more stable AHA^- dominated the ion population even at water to phenol concentration ratios bigger than 10^4. Recently we were able to produce the substituted phenoxide anions from the corresponding substituted anisols via the reaction $CH_3O^- + PhOCH_3 = PhO^- + CH_3OCH_3$. Preliminary results from the hydration equilibria measurements bear out the relationship between the basicity of A^- and the hydrogen bond energies in $A^-(HOH)_n$. We hope to be able to report on these results in the near future.

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