Intrinsic Acidities of Substituted Phenols and Benzoic Acids Determined by Gas-Phase Proton-Transfer Equilibria

T. B. McMahon and P. Kebarle*

Contribution from the Chemistry Department, University of Alberta, Edmonton, Canada T6G 2E1. *Received July 12, 1976*

Abstract: Gas-phase proton-transfer equilibria: $A_1H + A_2^- = A_1^- + A_2H$, involving some 50 benzoic acids and phenols and various other standard acids with known acidities were measured with a pulsed electron beam high ion source pressure mass spectrometer. The equilibrium constants K were used to obtain the free energy changes and establish the relative and absolute gas-phase acidities of the benzoic acids and phenols. The gas-phase acidities of the substituted benzoic acids and phenols are compared with the corresponding aqueous acidities. The reasons for the very different attenuation of the substituent effects in water and Me_2SO are examined. Ortho effects in the gas phase and specific hydrogen bonding effects are also discussed. The electron affinities of some phenolic radicals are determined from known bond dissociation energies and the gas-phase acidities.

Linear free energy relationships have had a profound impact on the development of physical organic chemistry. Thus the classification of substituent effects on chemical reactions done in connection with Hammett type plots led to many of the now widely used concepts of bonding and electronic effects.[1] The ability of phenols and benzoic acids to ionize as Brønsted acids in the experimentally easily accessible pH range made them the natural choice as references for free energy relationships.[2] The vast majority of reaction types, including the reference reactions that have been successfully correlated by linear free energy relationship plots, are processes occurring in solution. Since ionic solvation is an integral and dominant part of the energetics of these reactions, interpretations of free energy correlations purely in terms of electronic arguments involving the reactants but not the solvent has been a perennial area of concern. One pertinent example is the finding that in most cases the differences in free energy of ionization of substituted phenols and benzoic acids are due to a change of entropy.[3-7] Yet, if solvation effects are not taken into account, electronic effects of the substituents should show up in the enthalpy and not in the entropy change. To separate solvent effects from the intrinsic molecular effects of the substituents one needs to know the free energy and enthalpy change for the same process occurring in the dilute gas phase. Fortunately such data have recently become available from studies of gas-phase ion molecule reactions.[8] Information on the intrinsic acidities and basicities is obtained from studies of the gas-phase proton-transfer reactions

$$A_1H + A_2^- = A_1^- + A_2H \qquad (1)$$

$$B_1H^+ + B_2 = B_1 + B_2H^+ \qquad (2)$$

In earlier work[9,10] only the sign of the free energy change could be obtained from the observed occurrence or nonoccurrence of the reaction in the forward direction. Many important results on gas-phase acidity orders were obtained with this technique.[11-13] More recently, the study of ion equilibria[14] was extended to proton-transfer reactions in ICR mass spectrometers,[15] high-pressure pulsed ion sources,[16] and flowing afterglow apparatus.[17] The resulting determinations of K, $\Delta G°$, and $\Delta H°$ have provided already many significant data.

It is interesting to note that recently[18] results from ab initio MO methods using relatively simple STO-3G basis sets have predicted energy changes (ΔE_2) for the positive ion proton-transfer reactions (eq 2) which are in very good agreement with gas-phase ion equlibria data (ΔH_2). Thus an important independent contribution for these reactions can be expected from theoretical calculations. On the other hand the negative ion systems (eq 1) are electron crowded systems in which electron repulsion and electron correlation are much more important. These systems require much more accurate calculations, larger basis sets, and electron correlation corrections. Therefore, unfortunately, numerous and good theoretical calculations of ΔE_2 cannot be expected in the near future.[55a]

A brief report[19] on the gas-phase acidities of the monosubstituted benzoic acids was presented earlier from this laboratory. The present publication presents more extensive documentation of these early results and combines them with newly obtained results for the substituted phenols[20] in a more comprehensive treatment of substituent effects on the acidity of benzoic acids and phenols.

Experimental Section

The acidity data obtained in this work were measured using a pulsed electron beam high-pressure mass spectrometer, which has been described previously.[21] Briefly, a typical experiment is carried out as follows.

A concentrated methanol solution containing a known molar ratio of the two acids of interest is prepared by dissolving accurately weighed amounts of the acids into methanol. This solution is injected with a syringe through a septum into a 5-L bulb containing 1 atm of the buffer gas methane. NF_3 (50 cm^3) at 1 atm are also injected into the bulb. The bulb and inlet system to the ion source are maintained at 150–200 °C to ensure complete vaporization of the rather involatile benzoic acids and phenols. Typically the bulb contains 1 atm of methane, 3 Torr each of the acids of interest, and 10 Torr of NF_3. After allowing sufficient time for mixing, this gaseous mixture is passed in slow flow through the ion source. The flow out of the bulb is controlled by means of an all metal valve. The gas mixture flows through ~10 mm i.d. tubing in and out of the ion source and then passes via a flow control capillary into a pump. The pressure in the flow system and ion source is maintained at some constant value in the 2–5 Torr range. Viscous flow results under these conditions. Therefore no fractionation of the minor components (i.e., the acids) should occur and the partial pressure ratios of the acids in the ion source should be identical with those in the storage bulb. A confirmation of the expected lack of fractionation could be obtained by observing that the measured equilibrium constant K_1 changed by only 5% after 85% of the gas had flowed out of the 5-L storage bulb.

The ratio of the neutral acids in the bulb was varied by a factor from 2 to 5 in separate experiments where new methanol solutions were prepared and injected. The equilibrium constants were found to be independent of the concentration ratios used.

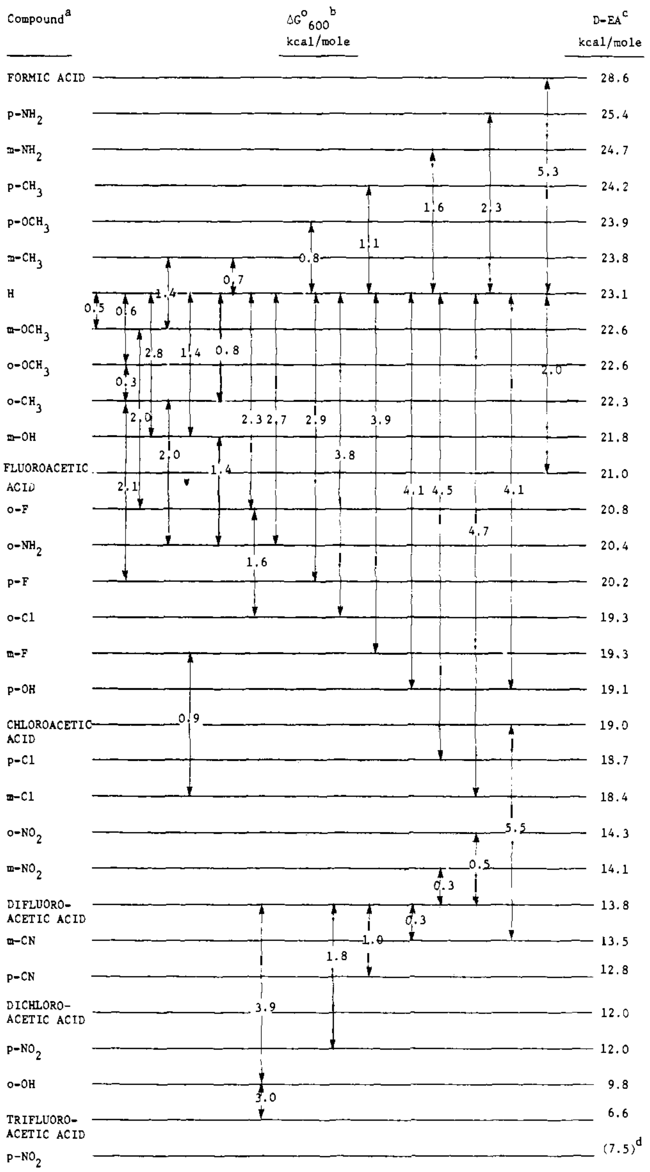
Ionization of the sample is accomplished by a short (~10 μs) pulse of 2000-eV electrons, which creates some 10^7 ions and electrons. The NF_3 undergoes dissociative electron attachment to produce F^-. The fluoride ion rapidly abstracts protons from the benzoic acids and phenols, which are stronger gas-phase acids than HF. The time required for the establishment of the equilibrium is short compared with the time accessible to observation. The F^- ion disappears within microseconds. The kinetic stage of reaction 1 lasts ~100 μs. After this time the ion intensity ratio A_1^-/A_2^- becomes constant and remains so for the whole period of observation (~5000 μs).

The reactants A^- suffer some 100 thermalizing collisions with buffer gas before colliding with either of the acid molecules. This should be sufficient to remove any excess energy in A^- due to the exothermicity of reaction 1.

The carboxylic acids AH are known to form hydrogen-bonded dimers $(AH)_2$ in the gas phase. An examination of the expected concentrations of $(AH)_2$ on the basis of available data on the monomer dimer equilibria data showed[22] that the dimer concentration is completely insignificant under the experimental conditions used.

At room temperature the thermodynamic equilibrium is not between the monomers A^-, but between the clustered ions $A^-(HA)_n$. In order to observe the monomer equilibrium (eq 1) the ion source had to be maintained at 600 K. The ions at this temperature are mostly A^- with some $(AHA)^-$. The presence of the AHA^- species does not disturb the measurement of the equilibrium 1. The dimerization reaction $A^- + HA = AHA^-$ is generally third-body dependent in the pressure range used and thus slower than reaction 1. Furthermore, following the time dependence of the dimers AHA^- it could be established that these soon (100-200 μs) reach equilibrium with the monomers A^-. In principle, the monomer equilibrium (eq 1) can be measured in the presence of a vast excess of AHA^-, also at equilibrium. However, this condition is to be avoided for instrumental reasons when high-pressure mass spectrometers are used. A small fraction of the ions, after leaving the ion source, suffer collisions with the neutral gas escaping from the ion exit slit. If the ions AHA^- were already accelerated by a few volts these collisions lead to dissociation to A^- + HA where the A^- is detected after mass analysis as of mass corresponding to A^-. This nonequilibrium signal leads to errors in the measurement of the relative A^- concentrations for conditions where AHA^- was by far the dominant ion in the ion source.

Table I. Free Energies of Proton Transfer for Gas-Phase Reactions $A_1H + A_2^- = A_1^- + A_2H$ Involving Substituted Benzoic Acids and Standard Acids



Compound[a]	D-EA[c] kcal/mole
FORMIC ACID	28.6
p-NH_2	25.4
m-NH_2	24.7
p-CH_3	24.2
p-OCH_3	23.9
m-CH_3	23.8
H	23.1
m-OCH_3	22.6
o-OCH_3	22.6
o-CH_3	22.3
m-OH	21.8
FLUOROACETIC ACID	21.0
o-F	20.8
o-NH_2	20.4
p-F	20.2
o-Cl	19.3
m-F	19.3
p-OH	19.1
CHLOROACETIC ACID	19.0
p-Cl	18.7
m-Cl	18.4
o-NO_2	14.3
m-NO_2	14.1
DIFLUOROACETIC ACID	13.8
m-CN	13.5
p-CN	12.8
DICHLOROACETIC ACID	12.0
p-NO_2	12.0
o-OH	9.8
TRIFLUOROACETIC ACID	6.6
p-NO_2	(7.5)[d]

[a] Acid used as standard for the determination of D − EA are given their full name, benzoic acids identified only by the substituent. [b] Free energy change at 600 K for reaction $A_1H + A_2 = A_1^- + A_2H$, ΔG°_{600} given beside double arrow connecting the two acids. Acid strength increases from top to bottom of the table, i.e., ΔG°_{600} is negative if A_1H in the table lies above A_2H. [c] D − EA corresponds to the difference between the bond dissociation energy D(A−H) and the electron affinity EA(A). Assumption is made that $\Delta S_1^\circ = 0$. The heterolytic bond dissociation energy $D(A^- - H^+)$, i.e., the proton affinity of A^-, can be obtained from D − EA by adding 313.6 kcal/mol = IP(H) since: $D(A^- - H^+) = D(A-H) - EA(A) + IP(H)$. [d] Estimated value, see ref 30.

Results and Discussion

(a) Results. The free energy changes for the proton-transfer reaction 1, ΔG_1° obtained by measuring the equilibrium constant K_1 at 600 K, are shown for the substituted benzoic acids in Table I, while Table II gives the measurements for the phenols. As discussed in greater detail in section f of Results and Discussion, $\Delta S_1^\circ \approx 0$ and therefore:[55b]

$$\Delta G_1^\circ(600\ \mathrm{K}) \approx \Delta G_1^\circ(298\ \mathrm{K}) \approx \Delta H_1^\circ \qquad (3)$$

The heterolytic bond dissociation energy $D(A^- - H^+)$ is equal to the proton affinity of A^-. $PA(A^-)$ can be represented by the quantities shown in the equation

$$D(A^- - H^+) = PA(A^-) = D(A-H) - EA(A) + IP(H) \qquad (4)$$

where EA and IP stand for electron affinity and ionization potential. Assuming that eq 3 holds exactly, one obtains from eq 4 the relationship[55b]

$$\Delta G_1^\circ = \Delta H_1^\circ = D(A_1-H) - EA(A_1) - D(A_2-H) + EA(A_2) \qquad (5)$$

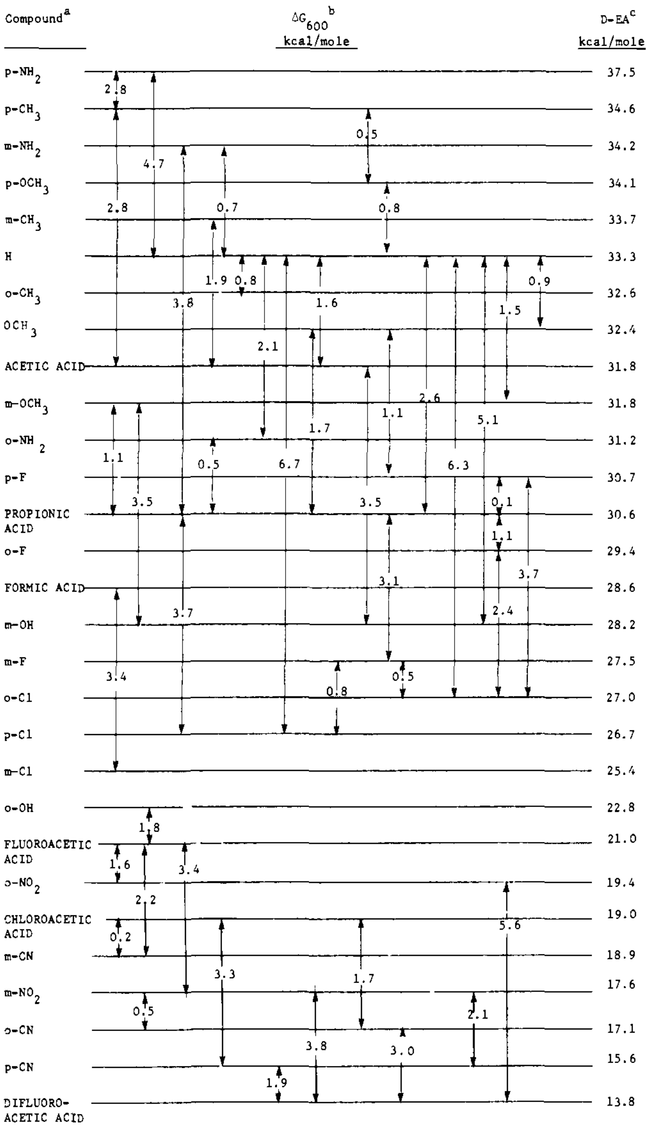
Since D(A-H) and EA(A) are known quite well for HCl and H_2S, equilibrium measurements (eq 1) involving the HCl and H_2S permit the evaluation of $PA(A^-)$ for other acids. In this manner the $PA(A^-)$ of several carboxylic acids were established earlier.[22] These acids were used in the present work as standards to which the $PA(A^-)$ of the benzoic acids and phenols were normalized. The Tables I and II contain the absolute acidities in the last column. However, since IP(H) is common to all $PA(A^-)$ (see eq 4) and IP(H) = 313.6 kcal/mol is a very large number which hinders quick comparison, we have given in the table only the quantity $D(A-H) - EA(A)$.

The internal consistency of the acidity measurements is demonstrated in Tables I and II by the various multiple thermodynamic cycles involving a given pair of acids. By inspection of the ΔG_1° values given in the tables, one can verify that the internal consistency is generally within ±0.4 kcal/mol. The error in the absolute $PA(A^-)$, i.e., D − EA, is probably considerably larger, i.e., around 2-3 kcal/mol.[55b]

In order to facilitate the examination of substituent effects, the data for the benzoic acids and phenols are also shown in Tables III and IV arranged according to the substituent.

McIver et al.[23] have reported some results for the substituted phenols. These data are shown in Table IV. The agreement with McIver's data is generally good, i.e., within less than 1

Table II. Free Energies of Proton Transfer for Gas-Phase Reactions $A_1H + A_2^- = A_1^- + A_2H$ Involving Substituted Phenols and Standard Acids

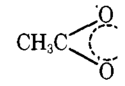


Compound[a]	D-EA[c] kcal/mole
p-NH_2	37.5
p-CH_3	34.6
m-NH_2	34.2
p-OCH_3	34.1
m-CH_3	33.7
H	33.3
o-CH_3	32.6
OCH_3	32.4
ACETIC ACID	31.8
m-OCH_3	31.8
o-NH_2	31.2
p-F	30.7
PROPIONIC ACID	30.6
o-F	29.4
FORMIC ACID	28.6
m-OH	28.2
m-F	27.5
o-Cl	27.0
p-Cl	26.7
m-Cl	25.4
o-OH	22.8
FLUOROACETIC ACID	21.0
o-NO_2	19.4
CHLOROACETIC ACID	19.0
m-CN	18.9
m-NO_2	17.6
o-CN	17.1
p-CN	15.6
DIFLUOROACETIC ACID	13.8

[a] Acids used as standard for the determination of $D - EA$ are given their full name, phenols are identified only by the substituent. [b,c] Same as footnotes in Table I.

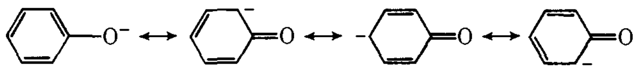
kcal/mol. Some of the differences undoubtedly are due to the different temperatures at which the two determinations were made and the failure of the assumption $\Delta S_1° = 0$. Unfortunately the chlorophenols show considerable disagreement. The largest discrepancy: *p*-chlorophenol, McIver, 2.9; present work, 6.6 kcal/mol, must reflect experimental error in one of the determinations. Examining the multiple cycles in Table II by which our *p*-chlorophenol was determined, we are inclined to believe that the error is not in the present determination.

(b) Comparison of Phenols and Benzoic Acids with Other Acids. Braumann and Blair[11] reported several years ago that the gas-phase acidity of phenol was much greater than that of simple aliphatic alcohols. The present data show that in fact phenol's acidity is comparable to that for acetic acid, and substituted phenols, such as *p*-nitrophenol, are as strong as the conventional strong organic acids. Since the acidity of phenol and acetic acid differ by nearly 6 pK_a units in aqueous solution[24] it is obvious that solvation effects play an important role in determining the relative solution acidities of these species. This is fairly easy to rationalize if one considers the nature of the anions to be solvated. In the case of the acetate anion (I)



I

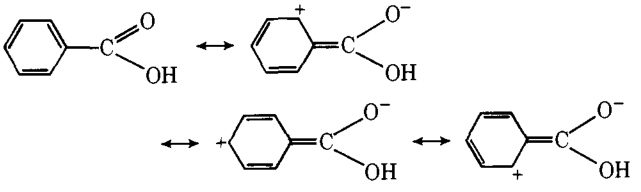
the negative charge is localized almost completely on the oxygen atoms, which provide excellent sites for solvation by protic solvents. Furthermore, the methyl group is small and will not impede much the approach of water molecules to the negative charge. On the other hand in the phenolate anion (II)



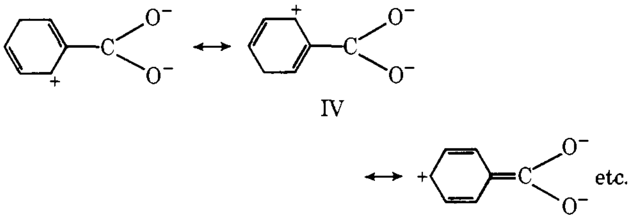
II

the negative charge may be delocalized throughout the aromatic ring. Such a delocalization of charge causes a lowering in total solvation energy which is particularly strong for protic solvents like water.[25] (For a comparison of the effect of charge delocalization on the solvation of anions by protic and aprotic solvents see section c.) Also, the phenyl group is large and leads to a large effective radius of the ion. The decreased solvation of the phenolate anion makes phenol a much weaker acid in solution.

Another example of the importance of solvation energies in determining aqueous acidities arises from a comparison of relative aqueous and gas-phase acidities of acetic acid and benzoic acid. In aqueous solution these acids have nearly the same pK_a, while in the gas phase benzoic acid is stronger by 8.7 kcal/mol. It has been shown[26] that resonance forms such as III are important in increasing benzoic acid stability in solution. The charge-separated structures will be more favorably solvated than the uncharged neutral molecule. The corresponding resonance structure for the benzoate anion (IV) will



III



IV

be considerably less important and thus the solvent stabilization of the neutral acid relative to the anion results in a lowering of the observed benzoic acid acidity in solution. In the gas phase charge-separated resonance forms are not as important, since they lack solvent stabilization and hence the benzoic acids are relatively much more acidic than acetic acid.

(c) Linear Free Energy Relationships and Solvation of Negative Ions by Protic and Aprotic Solvents. The substituent effects in the gas phase and their correlation with the substituent effects in solution can be most meaningfully examined on the basis of linear free energy plots. Such plots are shown in Figures 1-3. The plots in Figure 1 deal with substituent effects for benzoic acid. The σ^0 values on the left were obtained by Taft[26] from the ionization of substituted phenylacetic and phenylpropionic acids, while the $\bar{\sigma}$ values on the right represent data of Brown.[27] As pointed out in our earlier publication,[19] a somewhat better correlation of the gas-phase data is observed with σ^0 values. This may be rationalized on the basis of the decreased importance of charge-separated resonance structures

Table III. Gas-Phase Acidities[a]

Substituent	H	CH_3	OCH_3	OH	NH_2	F	Cl	CN	NO_2
				Benzoic Acids					
Ortho	23.7	22.9	23.2	9.8[c]	21.0	21.4	19.9		14.3
Meta	23.7	24.4	23.2	22.4	25.2	19.9	19.0	13.5	14.1
Para	23.7	24.8	24.4	19.6[c]	26.0	20.8	19.3	12.8	12.0
				Phenols					
Ortho	33.3	32.6	32.4	22.75	31.2	29.4	27.0	17.1	19.4
Meta	33.3	33.7	31.8	28.2	34.2	27.5	25.4	19.0	17.6
Para	33.3	34.55	34.05		37.5	30.7	26.7	15.6	(7.5)[b]

[a] Values in kcal/mol corresponding to $D(\text{A-H}) - \text{EA(A)}$, where D and EA are the bond dissociation energy and the electron affinity.[55b] The gas-phase acidity increases as $D - \text{EA}$ decreases. The proton affinity of A^- can be obtained by adding the ionization potential of hydrogen $\text{IP(H)} = 313.6$ kcal/mol to $D - \text{EA}$ (see eq 4). [b] Estimated value, see ref 30. [c] The *o,p*-hydroxybenzoic acids are actually *o,p*-carboxyphenols, since the hydroxy hydrogen is more acidic than the carboxy hydrogen (see text and ref 29).

Table IV. Substituent Effects on Gas-Phase Acidities of Benzoic Acids and Phenols[a]

Acid	Substituent	CH_3	OCH_3	OH	NH_2	F	Cl	CN	NO_2
Benzoic	Ortho	0.8	0.5	13.9	2.7	2.3	4.7		9.4
Phenol	Ortho	0.7	0.9	10.5	2.1	3.9	6.3	16.2	13.9
McIver[b]	Ortho	0.3				2.8	4.6		
Benzoic	Meta	−0.7	0.5	1.3	−1.5	3.8	4.7	10.2	9.6
Phenol	Meta	−0.4	1.5	5.1	−0.9	5.8	7.9	14.3	15.7
McIver[b]	Meta	−0.5				4.8	6.1		
Benzoic	Para	−1.1	−0.7	4.1	−2.3	2.9	4.4	10.9	11.7
Phenol	Para	−1.3	−0.8		−4.2	2.6	6.6	17.7	(25.8)[c]
McIver[b]	Para	−1.2				2.1	2.9		

[a] Values in kcal/mol correspond to $\Delta G°_{600}$ for reaction: $C_6H_5COOH + XC_6H_4COO^- = C_6H_5COO^- + XC_6H_5COOH$, and corresponding reaction between phenols. Acidifying substituents lead to positive $\Delta G°$ values. [b] Values for phenols obtained by McIver[23] measured at 298 K. [c] Estimated value, see ref 30.

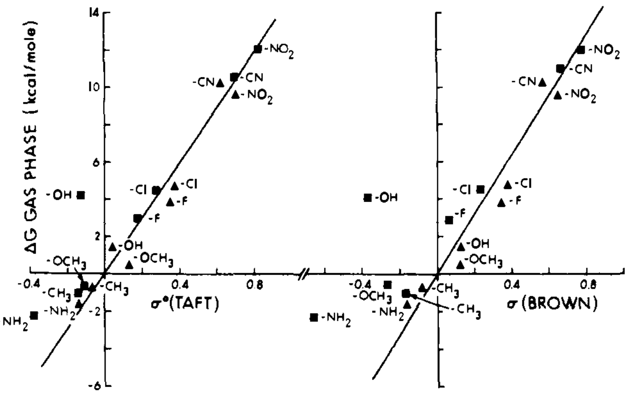
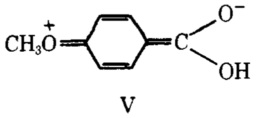


Figure 1. Correlation of gas-phase acidities of meta- ▲ and para- ■ substituted benzoic acids with σ and σ^0. The ΔG in the gas phase corresponds to free energy change for reaction: $XC_6H_4COO^- + C_6H_5COOH = XC_6H_4COOH + C_6H_5COO^-$. π donating substituents like CH_3O show better correlation in σ^0 plot.

in the gas phase relative to those in solution. Substituents which are π donating may stabilize the neutral benzoic acid by resonance structures such as V, which may be favorably solvated.



V

Using ^{19}F NMR techniques Taft[28] has shown that the electron density at fluorine in a number of para-substituted fluorobenzenes is markedly solvent dependent. In particular for +R substituents such as CO_2H, CO_2R, and NO_2 the electron density of fluorine is markedly reduced due to resonance structures such as VI. Since in the gas phase the solvent that

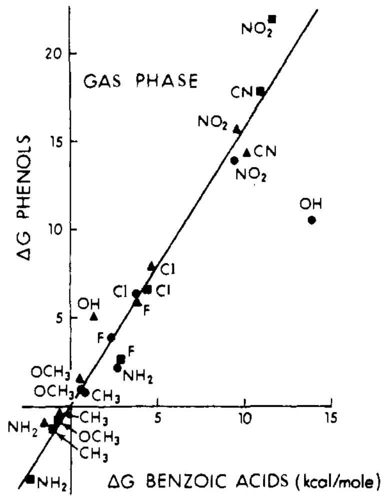
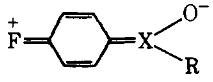


Figure 2. Comparison of gas-phase acidities of phenols and benzoic acids. The abscissa gives $\Delta G°$ for substituted phenols reaction: $XC_6H_4O^- + C_6H_5OH = XC_6H_4OH + C_6H_5O^-$, while the ordinate shows $\Delta G°$ for analogous reaction involving benzoic acids. Slope of the straight line is 1.5.



VI

X = C, N

R = OH, OR, O

promotes these structures is absent, their importance should be much smaller, although probably not negligible. Since the σ^0 constants were obtained with compounds where resonance shifts like those occurring in VI are not possible, the better

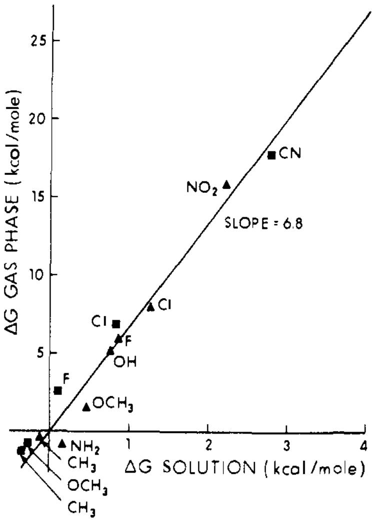
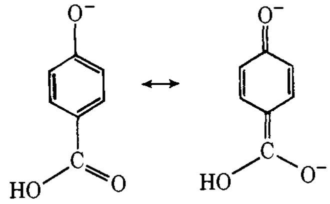


Figure 3. Comparison between gas-phase and aqueous acidities of substituted phenols. $\Delta G°$ shown in figure corresponds to free energy change for reaction $XC_6H_4O^- + XC_6H_5OH = XC_6H_4OH + C_6H_5O^-$: slope of straight line equals 6.8; △ meta; □ para substituents

agreement of the gas-phase acidities with the σ^0 constants is to be expected.

It is evident from Figure 1 that p-hydroxybenzoic acid has an anomalously high gas-phase acidity. From the σ values it would be expected that the p-OH substituent should lower the acidity by some 2 kcal/mol. Quite the contrary an increase of nearly 4 kcal/mol is observed. It can be shown[29] that in the gas phase the more acidic proton in p-hydroxybenzoic acid is not the carboxy but the hydroxy proton. Therefore the absence of fit in Figure 1 is due to the fact that we are not dealing with a benzoic acid but with a phenol. The greater acidity of the OH group can be understood when it is considered that the phenoxide ion receives the important resonance stabilization VII,



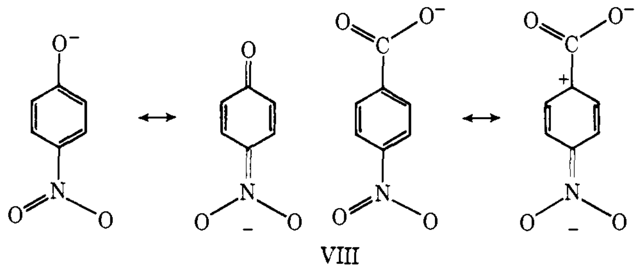
VII

while no equivalent stabilization by the OH group is available to the p-hydroxybenzoate anion.

The gas-phase acidities of the benzoic acids and phenols are compared in Figure 2. Apart from a few exceptions a good linear correlation is obtained. The reasons for the exceptions are easily understood. The large deviation for the o-OH substituent must be due to the fact that the o-hydroxybenzoic acid is not involved in the proton transfer but the o-carboxyphenol is; i.e., the situation should be the same as that considered[29] above for the para isomer. The ortho isomer is seen to be much more acidic than the para isomer (see Table III). This must be due to a stabilization of the ortho anion by an internal hydrogen bond between the COOH group and the O^-.

The p-nitrophenol is seen to have relatively higher acidity than predicted by the straight line. Such a deviation is also observed in solution and has been attributed to enhanced resonance effects for π-withdrawing substituents, which can conjugate directly with the negative charge of the phenolate anion. A similar deviation should have occurred also for p-cyanophenol. However, as can be seen from Figure 2 this positive deviation is too small to be significant. The p-nitrophenol value was obtained in an indirect way (see below) and is therefore somewhat uncertain. Therefore at present it is not possible to determine the extent of the direct conjugation effect.

The slope of the straight line in Figure 2 is equal to 1.5. The greater power of the substituents on the phenols must be connected with the fact that in the phenolate anions there is a more effective resonance interaction with the ring than for the benzoates. This is illustrated by the resonance structures VIII for the p-NO_2 anions.



VIII

The COO^- groups may be less sensitive to the electronic effects of the substituents also because the negative charge is distributed onto two oxygen atoms which are also somewhat farther removed from the ring.

The relationship between gas-phase and aqueous acidity of the m- and p-phenols is shown in Figure 3. As can be seen a good linear correlation is obtained. The good linearity of the plot was used to obtain an estimate for the gas-phase acidity of the p-nitrophenol[30] given in the tables.

It is interesting to note that the slope of the line in Figure 3 is 6.8; i.e., the substituent effect on the free energy change is 6.8 times larger in the gas phase than in aqueous solution. If the solution σ values of the benzoic acids in Figure 1 are converted to $\Delta G°$ values such that a plot equivalent to that shown for the phenols in Figure 3 is obtained, one finds an even larger slope of 10.6 for the benzoic acids. Attenuation of substituent effects from the gas phase to solution in situations where linear relationships exist[31] are common; however the attenuation for the phenols and particularly the benzoic acids is unusually large. Thus the basicities of substituted pyridines were found[32] to be attenuated by a factor of only about 3.6.

The difference between the attenuation of the benzoic acids and phenols is probably mostly due to the already considered weakening of aqueous acidities of benzoic acids due to the importance of the resonance stabilization (see structure III) of the neutral acids in polar solvents. After consideration of this effect we are still left with a large remaining attenuation by a factor of about 7 for both benzoic acids and phenols. Keeping in mind the relatively good quality of the linear relationships (see Figure 3) one realizes that the effect reducing the aqueous acidity must be (near) linearly dependent on the electronic effects of the substituents. The natural source of such an inverse compensation is the hydrogen bonding interaction of the anion A^- with the solvent. If the hydrogen bonds in the species $A^-\cdots(HOR)_n$ (we are writing HOR rather than HOH since the argument is common for all protic solvents) decrease as the acidity of AH increases, then the (partial) cancellation of the substituent effect in solution will be automatic. Considering the hydrogen bond as a "partial proton transfer", i.e., a partial acid-base reaction, a decrease of $A^-\cdots HOR$ bonding will be indeed expected as the basicity of A^- decreases, i.e., as the acidity of the conjugate acid AH increases. Studies of the hydrogen bond strength in various gas-phase complexes $A^-\cdots HOR$ have shown[33,34] that the hydrogen bond energy does in fact increase with the basicity of A^- and the acidity of HOR. A similar relationship[35-37] was also found for the positive onium ion species $R_1R_2R_3NH^+$ solvated by bases like OH_2. More directly significant to the present discussion is a recent gas-phase determination[38] of the binding enthalpies and free energies of phenolate anions to the protic "solvent" molecules HCl. These results[38] showed that the binding energies $XC_6H_4O^-$-HCl increase linearly with increasing basicity of $XC_6H_4O^-$ (i.e., with decreasing acidities of the phenols). Unfortunately, the experiments most directly pertinent to the present discussion showing that the hydrogen bond energies in the $XC_6H_4O^- \cdots (HOH)_n$ species increase with the basicity of the phenolate anions have not been done yet. However we are confident that this relationship will be soon confirmed.[39]

Of interest to the present discussion are also results obtained by Arnett[40] with the use of Born type cycles. These results allow a dissection of the substituent effect in solution into substituent effects: on the gas-phase ionization of the acids, on the solvation of the neutral acids, and on the solvation of the ions. Results from a recent application of this approach to the acidities of phenols are shown in Table V. The substituent effects in solution given by $\Delta G°_{H_2O}$ and $\Delta H°_{H_2O}$ reproduce Hepler's finding[3] that only a very small part of the $\Delta G°_{H_2O}$ appears in the $\Delta H°_{H_2O}$. This means that the substituent effect in solution is largely reflected in the entropy and not in the enthalpy. The $\delta \Delta H_h(A^-)$ given in the last column of Table V give the substituent effect on the total heat of hydration of the ion. Unfortunately, as explained by Arnett,[41] these $\delta \Delta H_h°(A^-)$ values are strongly affected by uncertainties in the available thermodynamic data and particularly the enthalpies of evaporation of the neutral acids AH. While these uncertainties make the detailed interpretation of the data difficult, the overall effect is quite clear. Almost all the favorable $\Delta G_{gas} \approx \Delta H_{gas}$ change due to an acidifying substituent is wiped out by an unfavorable effect of the same substituent on the $\Delta H°$ of hydration of the anion. For example *m*-Cl increases the gas-phase acidity by 7.9 kcal/mol, but decreases the hydration enthalpy of *m*-Cl-$C_6H_4O^-$ by a whole 9.3 kcal/mol. Similarly *p*-NO_2 increases gas-phase acidity by 25.8 kcal/mol and decreases solvation of the anion by 17.9 kcal/mol, and so on down the whole column. Some systematic changes of the energies of solvation and evaporation of the neutral acids occur also;[41] however, the overriding effect is the unfavorable change of ionic enthalpy of solvation. This is in line with the decrease of hydrogen bonding energies in $A^- \cdots (HOR)_n$ with increasing acidity of AH that was considered above. These results also answer the question concerning the appearance of the substituent effects in the entropy and not the enthalpy change. Since the weakened $A^-(HOR)_n$ bonding wipes out almost all the intrinsic ΔH effect of the acidifying substituent, the relatively greater disorder in the solvent possible in the vicinity of the substituted anion due to the weakened $A^-(HOR)_n$ interaction, results in a favorable and very noticeable entropy change.[42]

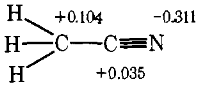
Bordwell et al.[44] have made recently a comparison between gas-phase acidities and solution acidities in Me_2SO. They found not only that gas-phase acidity orders are much more often preserved in Me_2 SO, but also that the solvent induced attenuation of the gas-phase substituent effects is quite small for Me_2SO. Included in Table V are the substituent effects on the acidities of phenols in Me_2SO. While there is a lot of scatter, the attenuation relative to the gas phase is seen to be small, probably something like a factor of 2. Another similarity between the behavior in Me_2SO and in the gas phase is given by the finding that the substituent effect in both cases is contained predominantly in the enthalpy change.

Table V. Free Energies and Enthalpy Changes for Reaction $XC_6H_4OH + C_6H_5O^- = XC_6H_4O^- + C_6H_5OH$ in the Gas Phase, Water, and Me_2SO[a]

X	$\Delta G_{gas} \approx \Delta H_{gas}$[b]	ΔG_{H_2O}[c]	ΔH_{H_2O}[c]	ΔG_{Me_2SO}[a] $\approx \Delta H_{Me_2SO}$	$\delta \Delta H_h(A^-)$[d]
o-CH_3	−0.7	0.5	0.22	−0.6	−0.4
m-CH_3	0.4	0.18	0.02	0.1	−0.7
p-CH_3	1.3	0.42	0.02	1.7	−2.2
o-Cl	−6.3	−1.9	−1.1	−4.5	
m-Cl	−7.9	−1.2	−0.3	−2.8	9.3
p-Cl	−6.6	−0.7	0.2	−1.5	10.9
p-NO_2	−25.8	−3.8	−0.8	−8.6	17.9

[a] Based on a recent publication by Arnett et al.[41] All values are in kcal/mol. [b] Gas-phase values used by Arnett[41] based on present work. [c] L. Hepler,[3] also P. D. Bolton and L. G. Hepler, *Q. Rev., Chem. Soc.*, **4**, 521 (1971). [d] $\delta \Delta H_h(A^-)$ corresponds to: $\Delta H_h(XC_5H_4O^-) - \Delta H_h(C_6H_5O^-)$, where ΔH_h is the total heat of hydration of the anion corresponding ΔH for transfer of the ion from the gas phase into liquid water. Values evaluated by Arnett.[41]

How can one understand the contrast between the behavior in water and in Me_2SO? Recent studies in the present laboratory[45] of the stabilities of gas-phase complexes between positive and negative ions and acetonitrile are pertinent to the above question. The positive ions were $Na^+ \ldots Rb^+$ and the negative ions $F^- \ldots I^-$. Acetonitrile is an aprotic solvent similar in many respects to Me_2SO. Electrostatic calculations[45] of the binding energies showed good agreement with the experimental results[45] and reproduced the experimental finding that the binding energies of acetonitrile to positive ions are much higher than to negative ions. These calculations showed that the weak bonding to negative ions is due to the very diffuse distribution of the positive pole of the acetonitrile dipole. Theoretically calculated atomic charge distributions for acetonitrile[4] are shown in structure IX. The very diffuse distribution of the positive charge in this molecule is evident. Obviously the center of the postive pole cannot be brought close to the negative ion. This leads to weak bonding.[47] The bonding is much better toward positive ions, since the negative pole of the dipole appears largely on the nitrogen for acetonitrile and the oxygen for Me_2SO.[48] Acidifying substituents on the phenols and benzoic acids are electron withdrawing groups that help transfer negative charge, in the anion, away from the acidic functional group. It is easy to see that molecules like Me_2SO and acetonitrile, which have a very diffuse distribution of their positive dipolar charge, will be very unsensitive to such charge dispersal. To make a comparison, they are like a hand in a thick mitt which cannot "feel" whether all the negative charge is located on the protuberant functional group or dispersed all over the anion. Therefore it can be expected that the solvation energy of the anion by such aprotic solvents will not be strongly decreased in the presence of charge dispersal. On the other hand the protic solvent molecules HOR are very much like a fine finger. The pinhead-like hydrogen carrying the total positive dipolar charge can interact directly with the functional group (CO_2^- or O^-) and is thus very sensitive to negative charge withdrawal from that group. Therefore charge dispersal in the anion A^- will cause a big decrease of solvation of the A^- and in acidity of AH in protic hydrogen bonding solvents.



IX

(d) Ortho Acidities. It has been recognized from the earliest investigations of structure-reactivity relationships that ortho-substituted benzene derivatives exhibit anomalous behavior. Ortho-substituted methyl- and methoxybenzoic acids are observed to have greater acidities than their para counterparts. This has been attributed in solution to be due to steric inhibition of resonance.[50] In solution resonance structures such as III stabilize the free acid and reduce the acidity. However,

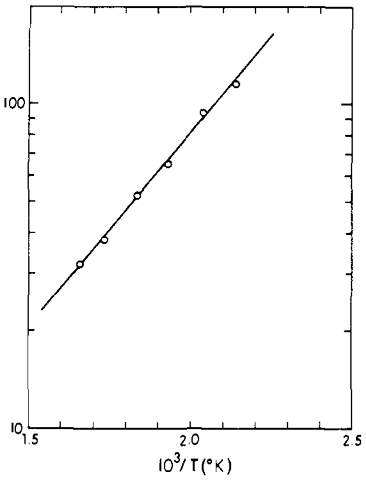


Figure 4. Temperature dependence of equilibrium $C_6H_5CO_2^-$ + $CH_2ClCOOH$ = C_6H_5COOH + CH_2ClCOO^- measured in the gas phase.

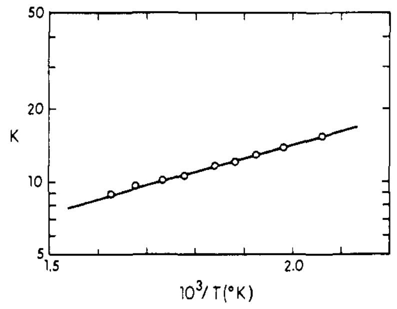


Figure 5. Temperature dependence of equilibrium $C_6H_5O^-$ + CH_3CH_2COOH = C_6H_5OH + $CH_2CH_2COO^-$ measured in the gas phase.

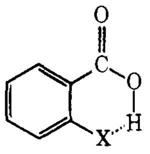
in the ortho position bulky substituents cause the carboxyl group to twist out of the plane of the aromatic ring and thus prevent resonance stabilization. As stated earlier, in the gas phase these resonance structures are much less important and thus the increase in ortho relative to para acidity should be much less than in solution. This is in fact the trend which is observed. However, it seems unlikely that the increased gas-phase acidity of ortho compounds relative to para can be entirely due to steric inhibition of resonance. As is frequently done in explanations of gas-phase acidities and basicities one must also consider the ion-induced dipole interaction between the anionic center and the substituent.[7,10] Consider, for example, *o*-methylbenzoic acid and assume that the negative charge in the anions is distributed equally between the two oxygens and that the center of polarizability is the methyl carbon. Then from

$$v(r) = -\alpha e^2/2r^4 \qquad (6)$$

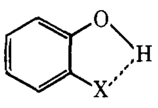
and assuming a C-O bond distance of 1.4 Å a maximum stabilization of 2.3 kcal/mol may be calculated for the carboxylate group in the plane of the ring and a minimum stabilization of 1.45 kcal/mol for the group perpendicular to the ring. Experimentally it is observed that the acidity of *o*-methylbenzoic acid is higher by 1.9 kcal/mol than the acidity of the para isomer. Thus it seems likely that for the methyl case the polarization interaction can account for the difference.

In substituted phenols there can be no steric inhibition of resonance in the neutral molecules and thus it would be expected that polarization interactions should account for increased ortho acidities. For example, in *o*-methylphenol, assuming a distance of 2.5 Å from the methyl group to the phenolate oxygen, a stabilization of 8.3 kcal/mol relative to *p*-methylphenol is calculated from eq 6. The observed difference is 2.0 kcal/mol. This large discrepancy may be rationalized on the basis of charge delocalization from the oxygen into the ring. Thus if roughly one-half of the charge is on the oxygen a stabilization of ~2 kcal/mol of *o*-methyl- relative to *p*-methylphenol would be expected.

While the above arguments may be used to explain the effects of *o*-methyl and *o*-methoxy substituents semiquantitatively, they fail to explain the acidities of *o*-halobenzoic acids and phenols. It would be expected on the basis of polarization interactions that ortho-substituted fluoro and chloro acids would be more acidic than the corresponding para-substituted compounds. In fact this is observed only for the fluorophenols. This result may be rationalized on the basis of intramolecular hydrogen bonding such as that shown in structures X and XI.



X



XI

Molecular models show that the geometry is most favorable for hydrogen bond formation in the *o*-halobenzoic acids and *o*-chlorophenol and that hydrogen bond formation is not likely in *o*-fluorophenol. It is then likely this stabilization of the neutral species by intramolecular hydrogen bonds that leads to higher para than ortho acidities in the gas phase.

In some cases stronger intramolecular hydrogen bonds may form, in which case ortho effects are much more pronounced. The nitro-substituted compounds bear a formal negative charge on the nitro oxygens and thus a relatively strong hydrogen bond forms in the neutral ortho-substituted benzoic acid and phenol. This is shown in the differences of 2.3 kcal/mol for *o*- and *p*-nitrobenzoic acids and of about 12 kcal/mol in the phenols.

In cases where intramolecular hydrogen bonding occurs in the anion ortho acidities are observed to be greatly enhanced. For example *o*-aminobenzoic acid is 5 kcal/mol stronger than *p*-aminobenzoic acid and *o*-aminophenol is more than 6 kcal/mol stronger than *p*-aminophenol. As mentioned previously *p*-hydroxybenzoic acid ionizes from the phenolic part of the molecule. Similar behavior is to be expected from the ortho compound and here the ortho compound is nearly 10 kcal/mol stronger than the para. Similarly, the estimated difference between *o*-hydroxy- and *p*-hydroxyphenol is about 11 kcal/mol.

(e) Electron Affinities of the Phenoxy Radicals. As shown in eq 4 the gas-phase acidity of a molecule may be directly related to the bond dissociation energy and radical electron affinity. If either of these quantities are known the other may be determined from the acidity data tabulated here. Mahoney has recently determined the O-H bond dissociation energies in a number of substituted phenols.[51] These values together with the electron affinities inferred from the acidity data of Table III are summarized in Table VI.

The electron affinity of the unsubstituted phenoxy radical obtained from $D - EA = 33.3$ kcal/mol[55b] and $D = 88.3$ kcal/mol from Mahoney[51] is EA(C_5H_5O) = 55 kcal/mol, while Westmore's[52] value of $D = 89$ kcal/mol leads to EA(C_6H_5O) = 55.7 kcal/mol. The average of these two values, 55.4 kcal/mol, is given in Table VI. This result agrees well with a value EA(C_6H_5O) = 54.4 kcal/mol obtained by Brauman[53] from the electron photodetachment threshold of the phenoxide ion $C_6H_5O^-$.

It is interesting to note that the electron affinity of the phenoxy radical is some 30% larger than that of OH (EA(OH)

Table VI. Electron Affinities of Phenoxy Radicals[a]

Compound	D(AH) − EA(A)[b]	D(A–H)[c]	EA(A)[e]
Phenol	33.3	88.3,[c] 89[d]	55.4 (54.4)[f]
p-Methylphenol	34.6	86.5[c]	52.0
p-Methoxyphenol	34.0	84.0[c]	50.0
m-Hydroxyphenol	28.2	90.9[c]	62.7

[a] All values in kcal/mol.[55b] [b] This work, see Table II. [c] L. R. Mahoney, private communication. [d] Fine and Westmore.[52] [e] Determined from D(AH) − EA(A). [f] J. H. Richardson, L. M. Stephenson, and J. T. Brauman,[53] determination of the electron photodetachment threshold of the phenoxide ion $C_6H_5O^-$.

= 42 kcal/mol),[54] reflecting the strong stabilizing effect of delocalization of the negative charge into the aromatic ring.

The two factors that will result in an increase of intrinsic acidity are a decrease of the bond energy and an increase of the electron affinity. As may be seen from the limited data for the substituted phenols (Table VI), the increase in acidity is entirely due to an increase of electron affinity; in fact the bond dissociation energies for the cases available are seen to change exactly in the opposite direction, i.e., they increase with increase of acidity. Thus it is due to the fact that the increase in electron affinity is larger than the increase in bond energy that higher acidity results for these species.

It is indeed unfortunate that so little independent data are available for changes of bond dissociation energies with substitution. The full thermochemical value of the present large store of D − EA data will become realized only when more independent bond dissociation energies and electron affinities become available.

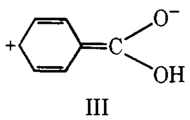
(f) Entropy Changes in the Gas Phase. The $\Delta H_1°$ values for the proton-transfer reactions 1: $A_1H + A_2^- + A_2H$, were obtained under the assumption that $\Delta S_1°$ is small, such that $\Delta G_1° = \Delta H_1°$.

Shown in Figures 4 and 5 is the measured temperature dependences for the equilibrium constants K of the reactions

$$C_6H_5CO_2^- + CH_2ClCO_2H \rightleftharpoons CH_2ClCO_2^- + C_6H_5CO_2H \quad (7)$$

$$C_6H_5O^- + CH_3CH_2CO_2H \rightleftharpoons CH_3CH_2CO_2^- + C_6H_5OH \quad (8)$$

From these data the thermochemical values $\Delta H_7° = -5.3 \pm 0.1$ kcal/mol, $\Delta S_7° = -2.0 \pm 0.2$ eu, and $\Delta G_7°(600\ K) = -4.1 \pm 0.1$ kcal/mol, and $\Delta H_8° = -2.6 \pm 0.1$ kcal/mol, $\Delta S_8° \leq 0.2$ eu, and $\Delta G_8°(600\ K) = -2.6 \pm 0.1$ kcal/mol, can be obtained. The entropy change for the phenol/propionic acid system is very nearly zero and thus the assumption that ΔG is equal to ΔH is an excellent one here. In the benzoic acid/chloroacetic acid case the entropy change of 2 eu causes a difference of 1.2 kcal/mol between the enthalpy change in reaction 7 and the measured free energy change. Furthermore, there is a difference of 0.6 kcal/mol between $\Delta G_7°(600)$ and $\Delta G_7°(300)$. The most likely cause of the entropy change observed for reaction 7 are rotational barriers. The neutral product is benzoic acid, for which the resonance structure III,



III

if important, will induce a rotational barrier about the phenyl-CO_2H bond. As discussed in the preceding sections the results indicate that III being charge-separated is not important in the gas phase. Therefore it is unlikely that the 2 eu could be due only to this rotational barrier. The ionic product in reaction 6 is $CH_2ClCO_2^-$. The electrostatic repulsion between the partial negative charge on the chlorine and the negative charge on the oxygen atoms could create a rotational barrier of a few kilocalories height. Thus the combined effect of the barriers in both products might be responsible for the loss of two entropy units in reaction 7.

The systematic study of entropy effects in reactions like 7 and 8 is obviously desirable and of interest not only from the standpoint of improving the value of the thermochemical data, but also for the purpose of obtaining information on rotational barriers caused by resonance effects, electrostatic repulsions, and other factors. Unfortunately such measurements are time consuming and sometimes difficult because of the abundant formation of AHA^- at lower temperatures. Furthermore the error in the entropy determinations should be less than 1 eu, an accuracy that might be difficult to achieve in a narrow temperature interval. We intend in future work to attempt more such temperature studies. For the present one must settle for a possible uncertainty between $\Delta G°_{600}$ and $\Delta G°_{300}$ of about 1 kcal and a difference between $\Delta G°_{300}$ and $\Delta H°_{300}$ of the same magnitude.[55b]

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(30) Unfortunately *p*-nitrophenol decomposed at the high ion source temperature (600 K) used in the experimental equilibria measurements. The gas-phase acidity of this compound can be estimated from the plot in Figure 3 using the known pK_a for aqueous *p*-nitrophenol. This leads to a $\Delta G°$ = 12.8 kcal/mol for the gas-phase proton transfer $p\text{-}NO_2C_6H_4O^- + C_6H_5OH = p\text{-}NO_2C_6H_4OH + C_6H_5O^-$. Combining this with D(A–H) − EA(A) for phenol this leads to D(A–H) − EA(A) = 7.5 kcal/mol for *p*-nitrophenol.
(31) Linear free energy relationships of substituent effects on gas phase and

aqueous solution proton transfer can be expected for the following conditions: (a) volume of moiety is large compared with the volume of the substituent; (b) electron directing power of the substituent is strong; and (c) substituent does not replace a hydrogen atom which could formerly engage in strong hydrogen bonding to the solvent.

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(39) Experiments to measure the binding energies $XC_6H_4COO^-$–HOH are presently under way. The experimental difficulty in series of this type is that the phenolate or benzoate anion A^- should not be produced by proton abstraction from the respective acid, AH, since in the presence of AH the major proton held dimers are AHA^- and not A^-HOH even when a large excess of HOH is used. This again is a consequence of the hydrogen bond following the acidity. The acidity of the phenols and benzoic acids being much larger than that of HOH leads to the dominance of the AHA^- clusters.

(40) See, for example, E. M. Arnett, F. M. Jones III, M. Taagepera, S. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Am. Chem. Soc.*, **94**, 4724 (1972).

(41) E. M. Arnett, L. E. Small, D. Oancea, and D. Johnston, *J. Am. Chem. Soc.*, submitted for publication.

(42) The above discussion of the substituent entropy effects in aqueous solution was conceived by the present authors on the basis of the mentioned studies of hydrogen bonding $A^- \cdots$ HOR in the gas phase. An examination of the literature showed that similar ideas were expressed earlier.[3] Repetition of the argument in the present form is thought to be useful, since its acceptance does not seem to be widespread.[43]

(43) T. M. Krygowsky and W. R. Fawcett, *Can. J. Chem.*, **53**, 3622 (1975).

(44) F. G. Bordwell, J. E. Bartmess, G. E. Drucker, Z. Margolis, and W. S. Matthews, *J. Am. Chem. Soc.*, **97**, 3226 (1975).

(45) W. R. Davidson and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 6125 (1976).

(46) W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 2191 (1970).

(47) The error introduced by the point dipole approximation used in conventional electrostatic calculations increases with the distance over which the actual charges of the molecule are distributed. A conventional correction is to use higher moments like quadrupole moment, etc. However, the use of net atomic charges as in structure IX is a method that is satisfactory and is more natural to the chemist.

(48) Good theoretical ab initio calculations[49] of $M^+ \cdots OH_2$ ($M^+ = Li^+ \ldots Cs^+$) have shown that the bonding is essentially electrostatic. Thus, Mulliken population analysis showed[49] that there is an electron transfer of only 0.018 and 0.004 e from the water molecule to the Li^+ and K^+ ions, respectively. Therefore application of the Lewis acid/base concept to systems like K^+ and OH_2 with the implied sharing of the pair donated by the base is not helpful, but rather misleading. The situation should be very similar for acetonitrile and Me_2SO.

(49) E. Clementi and H. Popkie, *J. Chem. Phys.*, **57**, 1077 (1972); H. Kistenmacher, H. Popkie, and E. Clementi, *ibid.*, **58**, 1689 (1973); **59**, 5892 (1973).

(50) J. Hine, "Physical Organic Chemistry", McGraw-Hill, New York, N.Y., 1962.

(51) L. R. Mahoney, private communication.

(52) D. H. Fine and J. B. Westmore, *Chem. Commun.*, 273 (1969).

(53) J. H. Richardson, L. M. Stephenson, and J. T. Brauman, *J. Chem. Phys.*, **62**, 1580 (1975).

(54) L. M. Branscomb, *Phys. Rev.*, **148**, 11 (1966).

(55) NOTE ADDED IN PROOF. (a) The prognosis about the propable inapplicability of the ΔE calculations (with STO-3G basis sets) to the isodesmic reactions (eq 1) involving negative ions has proven incorrect. Radom has published such calculations using the closed-shell procedure. In fact Radom's publication includes calculations for proton transfer between some substituted phenols that are generally in good agreement with results in Table IV (L. Radom, *J. Chem. Soc., Chem. Commun.*, 403 (1974)).

(b) A recent reexamination[56] of the assumption $\Delta S^\circ{}_1 \approx 0$ for the reactions (eq 1) involving proton transfer in negative ions has shown that the resulting error introduced in the $\Delta H^\circ{}_1$ can be significant. In particular the reaction: $Cl^- + AH = HCl + A^-$, which involves our primary standard HCl, generally has a $T\Delta S^\circ \approx$ 2–3 kcal/mol at 600 K because of the appearance of two (external) rotations in HCl which are generally only partially canceled by disappearance of (internal) rotations in $AH \rightarrow A^-$. For this reason the $D(AH) - EA(A)$ values given in Tables III and VI are generally too low by about 2 kcal/mol. For example, the new[57] $D - EA$ for phenol is 34.6 ± 2 kcal/mol and not 33.3 kcal/mol as shown in Tables III and VI.

(56) J. B. Cumming and P. Kebarle, *J. Am. Chem. Soc.*, to be submitted for publication.

Regio- and Stereoselectivity of Chiral Binaphthyl Reductive Aminoalkylation. Rotational Conformation and Electron Distribution of Alkali-Metal Biarylides

O. Eisenstein,[1a] J. P. Mazaleyrat,[1b,d] M. Tordeux,[1c] and Z. Welvart*[1b]

Contribution from the Groupe de Recherche No. 12 and C.E.R.C.O.A., C.N.R.S.,
94320 Thiais, France, and Laboratoire de Chimie Théorique, Bat. 490,
91405 Orsay, France. *Received June 7, 1976*

Abstract: The reductive aminoalkylation of 1,1′-binaphthyl by alkali metals and aminonitriles occurs in position 4. According to Hückel calculations, the high regioselectivity and the lack of asymmetric induction, when the reaction is performed with chiral binaphthyl, are in agreement with a flattened intermediate alkali metal binaphthylide. The product obtained by deuterolysis is *trans*-4-aminoalkyl-3-deuterio-3,4-dihydro-1,1′-binaphthyl. The high stereoselectivity of the deuteration and its regioselectivity in an unusual position can be explained by an orbital overlap stabilization of the transition state.

The reactivity of the alkali-metal biphenylide was uncertain for a long time[2,3] as shown by the conflicting results reported on the reduction of the parent hydrocarbon.[4] But a recent work of Harvey et al.[5] proves that this reagent behaves like radical anions derived from other aromatics. These react where electron density is highest and this can be determined by simple Hückel calculations.[2,6-8]

However other problems concerning the reactivity of radical anions formed from diaryl-type aromatic hydrocarbons also have to be elucidated.

(1) The electron distribution in these compounds is conformation dependent and it has been suggested that the twisting of the neutral molecule and of the corresponding radical anion and radical cation could be different.[9] The twisting of the radical anions has to be taken into account in a study of their reactivity.

(2) Some of these aromatics are chiral, and it is therefore worthwhile to examine if in the corresponding radical anion reactions asymmetric induction occurs. Only very few results concerning the properties of chiral radical anions have been reported.[10]

These problems are examined in the present work and 1,1′-binaphthyl, an easily resolvable aromatic hydrocarbon,[11] is used. The reaction studied is a reductive aminoalkylation[12,13] which involves radical anion intermediates similarly to the alkali-metal reductions[2,3,6-8] and the reductive alkyla-