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Intrinsic Acidities of Carbon and Nitrogen Acids Measured by Gas Phase Proton Transfer Equilibria. Substituent Effects on the Stabilities of Gas Phase Carbanions and Nitrogen Anions

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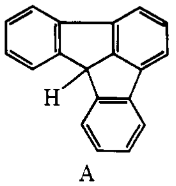
Abstract: Relative and absolute gas phase acidities of a number of carbon and nitrogen acids have been determined. In many cases relative acidities in sharp contrast to solution data are observed. This leads to information concerning intrinsic substituent effects on gas phase acidity and the importance of solvation energies in determining solution acidities. The effects of charge delocalization, inductive effects, aromaticity, and molecular conformation on acidity are discussed. Use of acidity data in determining thermochemical properties is demonstrated and electron affinities of a variety of organic free radicals are presented. The relative influence of substituents on electron affinity and hence negative ion stability is discussed.

The study of the gas phase chemistry of ionic species is of considerable importance since it allows an assessment of intrinsic molecular properties in the absence of complex interactions with solvent molecules. In particular the properties of gas phase carbanions are of interest since in solution carbanions are extremely useful synthetic intermediates which generally exhibit high reactivity. This high reactivity is generally interpreted to indicate that carbanions are unstable species. However, theoretical calculations[2] and recent gas phase experiments[3-5] indicate that a wide variety of carbanions are more stable than a number of other anions which are generally regarded as stable solution entities. For example, the benzyl anion may be readily generated in the gas phase by proton transfer from toluene to methoxide ion even though in solution the pK_a of toluene is 15 pK_a units greater than methanol.[3,4] This striking reversal of gas phase solution reactivity is an excellent indication that solvation phenomena may play a dominant role in determining solution properties and reactivities of ionic species. It has also been shown that frequently different solvents will cause a molecule to exhibit different relative acidity. An example of such a situation is fluoradene (A) which produces an anion with a high degree of charge delocalization. In dimethyl sulfoxide, a polar aprotic solvent, fluoradene, is found to have a pK_a of 10.5 while in methanol, a protic solvent, it has a pK_a of 17.[6] This large change is a result of the change in the nature of the solvation process. Such results make it essential that the properties of unsolvated ions be examined. The determination of the gas phase acidities of molecules RH leads[7] to values for the difference between the bond dissociation energy and the electron affinity: $D(\mathrm{R{-}H}) - \mathrm{EA(R)}$. In cases where either $D(\mathrm{R{-}H})$ or EA(R) are known from other sources the remaining quantity can be determined. The thermochemical information obtained in this manner is often very useful.


A

In the present paper we describe measurements of gas phase acidity for several compounds which are known to readily yield carbanions in solution and for a few compounds such as 1,4-pentadiene, diphenylmethane, acetone, and acetonitrile which are usually thought of as extremely weak solution acids. In addition a number of nitrogen acids were also examined. These latter experiments produced a number of gas phase nitrogen anions which are rarely, if ever, postulated in solution. The resulting comparison of substituent effects on stabilities of carbanions and nitrogen anions provides a means of assessing the relative importance of factors contributing to anionic stability.

Experimental Section

The experiments carried out in the present study were conducted using the pulsed electron beam high-pressure mass spectrometer which has been described in detail elsewhere.[8] Only a brief description of the apparatus and techniques will be given here.

All experiments involved binary mixtures of the particular acid under study with some reference acid. Each mixture was prepared by weighing certain amounts of each material, dissolving the two in methanol, and injecting a portion of the solution into a 5-l. bulb filled to 1 atm with methane. A known amount of SO_2F_2 or NF_3 was also added to the bulb to enhance negative ion formation. The bulb and gas inlet system are enclosed in a thermostated chamber maintained at some fixed temperature between 150 and 200 °C to ensure complete vaporization of all materials. Typical partial pressures in the bulb were 700 Torr of methane, 1-5 Torr each of the particular acid and reference compound, 50 Torr of methanol, and 10 Torr of SO_2F_2 or NF_3. This gaseous mixture is bled by means of an all metal control valve into a flow system part of which is the high pressure ion source maintained at approximately 325 °C by means of heaters installed in the ion source block. The valve is adjusted to give some constant total pressure in the ion source.

Ion source pressures between 8 and 0.5 Torr were used. A pulsed beam of electrons accelerated by 2000 V and of 10-20 μs duration produces F^- by dissociative attachment of electrons to SO_2F_2 or NF_3. The fluoride ion rapidly produces the anions of interest by the reaction $F^- + HR = HF + R^-$. Each ion undergoes several thousand collisions while diffusing through the field free ion source toward the walls. Ions which come near the region of molecular flow near the exit slit escape into the high vacuum region (10^{-4} Torr) where they are accelerated, magnetically mass analyzed, and detected by an electron multiplier detector. The electron beam pulse and a multichannel scaler are synchronously gated approximately every 5 ms. Using dwell time of 10 μs/channel it is thus possible to observe the temporal variation of ion intensities for nearly 3 ms. This is usually sufficient time for the system to reach thermodynamic equilibrium and thus from the steady state ion abundance ratio and the known composition of the gas mixture it is possible to obtain equilibrium constants and accurate free energies of reaction. Typically data are collected for 60 s per ion, but in cases of unusually low signal intensities such as with the weakest acids, collection times of 120 or 240 s per ion were occasionally used.

The temperature of the ion source block is variable from room temperature to approximately 400 °C. In order to minimize clustering processes all equilibrium data were recorded at relatively high temperature (327 °C). In cases where it was desired to examine temperature dependence of equilibria to ascertain entropy effects the temperature was varied between 225 and 327 °C.

Results and Discussion

1. Equilibria Data. The relative gas phase acidities of two compounds R_1H and R_2H may be readily measured in the high-pressure mass spectrometer by observing the steady state ion abundances, R_1^- and R_2^- in the equilibrium, of reaction 1 where the ratio of partial pressures, R_1H/R_2H, is known and the ion ratio is determined mass spectrometrically.[5,7,9,10]

$$R_1^- + R_2H \rightleftharpoons R_1H + R_2^- \qquad (1)$$

The gas phase acidity of a compound may be conveniently connected to other useful thermochemical quantities as shown in reaction 2. The proton affinity of the conjugate base, R^-,

$$\begin{tikzcd} RH \arrow[r, "D(R\text{-}H)"] \arrow[d, "PA(R^-)"'] & R + H \arrow[d, "-EA(R)"] \\ R_1^- + H^+ \arrow[r, "I_p(H)"] & R_1^- + H \end{tikzcd} \qquad (2)$$

serves as a practical measure of the acidity of RH (eq 3). Since

$$PA(R^-) = D(R\text{-}H) - EA(R) + I_p(H) \qquad (3)$$

the ionization potential of hydrogen atom, $I_p(H) = 313.6$ kcal/mol, is common to this expression for all compounds RH and since its value is very large, it has been our practice to omit this constant quantity from previous tabulations of data. Thus our relative measure of the acidity is the enthalpy for reaction 4.

$$e + RH \longrightarrow R^- + H \qquad (4)$$

$$\Delta H_4{}^\circ{}_{(298\,°C)} = D(R\text{-}H) - EA(R) \qquad (5)$$

From this formalism it can readily be seen that the difference in gas phase acidities of two compounds R_1H and R_2H is given by eq 6. The enthalpy $\Delta H_1{}^\circ$ can be connected to the

$$\Delta H_1{}^\circ{}_{(298\,°C)} = D(R_2\text{-}H) - EA(R_2) - [D(R_1\text{-}H) - EA(R_1)] \qquad (6)$$

experimentally determined ΔG° by eq 7. Furthermore since

$$\Delta G = \Delta H - T\Delta S \qquad (7)$$

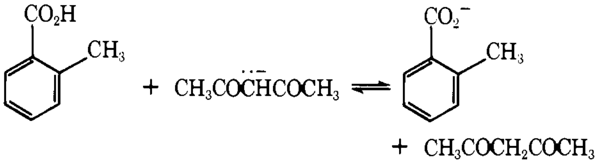
ΔS_1 is generally small, i.e., less than 2 eu (see next section), the assumption $\Delta G_1{}^\circ \approx \Delta H_1{}^\circ$ is made.

Absolute values of gas phase acidity of the compounds of interest are then assigned from a series of multiple thermodynamic cycle experiments which include one or more standard reference compounds for which both the bond dissociation energy and electron affinity are well established. In this study most carbon and nitrogen acids were measured relative to benzoic acids[10,11] and phenols[11] which in turn have previously been assigned absolute values of acidity on the basis of experiments with HCl and H_2S.[7,9]

The compounds examined in this work together with their assigned value of acidity and the values of ΔG obtained for each equilibrium examined are shown in Figure 1. These multiple cycle experiments lead to an internal consistency of ±0.2 kcal/mol for all values of acidity except the five weakest acids which exhibited very low ion signals. Even in these cases, however, the internal consistency is within ±0.5 kcal/mol. The absolute accuracy of the acidity scale established here is demonstrated by the excellent agreement between the value which we obtain for cyclopentadiene and that calculated from literature values for the C-H bond energy and the cyclopentadienyl radical electron affinity.[5] On this basis an absolute accuracy of ±2 kcal/mol may be confidently applied to this scale.

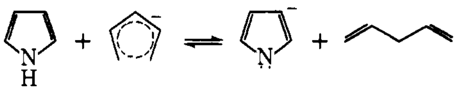
2. Entropy Effects. The charge delocalization which stabilizes substituted carbanions and nitrogen anions often freezes out or restricts internal rotations because of partial double bond formation. This loss of internal degrees of freedom would lead to significant entropy changes associated with proton transfer.

In order to investigate these potential sources of entropy effects we have examined the temperature dependence of ΔG of proton transfer for mixtures of acetylacetone-*o*-toluic acid and pyrrole-1,4-pentadiene. In the case of acetylaetone it was felt that upon formation of the anion resonance delocalization of charge would "freeze out" the two internal rotations about the CH-CO bonds and lead to a negative entropy change. However, examination of the temperature dependence of reaction 8 between 225 and 327 °C revealed that ΔS for proton transfer is very close to zero. As discussed later in this paper it seems likely that due to a combination of steric requirements and dipole-dipole repulsions there is no significant change in the freedom of internal rotation in proceeding from acetylacetone neutral to anion. It seems likely then that there is also no inherent entropy effect for transfer of a proton between a carboxy and a β-dicarbonyl carbon acid.



(8)

Similarly in pentadienyl anion the possibility that restriction of internal rotation would lead to negative entropy changes was considered. It has been shown from theoretical calculations that the charge is distributed nearly evenly on the first, third, and fifth carbons in pentadienyl[2] anion and from experiment that a U shaped carbanion is most probable.[12] However, examination of ΔG for reaction 9 between 245 and 327 °C revealed no temperature dependence and hence no measurable entropy effect (≤2 eu). The reason for lack of entropy effects in this reaction is not well understood.



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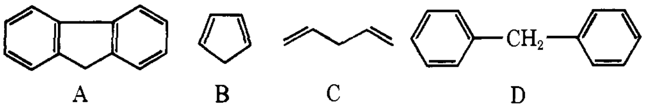
On the basis of failure to observe any significant entropy effects in these two reactions we assume $\Delta S \approx 0$ for all equi-

Table I. Hydrocarbon Acidities



Species	D(RH) − EA(R), kcal/mol	pK_a
A Fluorene	34.9	23
B Cyclopentadiene	39.1	15
C 1,4-Pentadiene	46.1	
D Diphenylmethane	47.0	35

Table II. Nitrile Acidities

Species	D(RH) − EA(R), kcal/mol	pK_a[a]
Malononitrile $CH_2(CN)_2$	17.2	12
Phenylacetonitrile $PhCH_2CN$	35.1	
Acetonitrile CH_3CN	47.9	25

[a] McEwen–Streitwieser–Applequist–Derry (MSAD) pK_2 scale: D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, N. Y., 1965.

libria examined here and use all free-energy values obtained as enthalpies of reaction. However, it is likely that entropy effects will in some cases lead to changes of the assumed ΔH values. At present we feel that the data obtained are sufficiently interesting to justify the uncertainty incurred by the nonexecution of the numerous and sometime difficult temperature measurement.

3. Hydrocarbon Acidities. The gas phase acidities of hydrocarbon species determined in this work are shown in Table I. The fluorenyl and cyclopentadienyl anions satisfy the criterion for aromaticity and as might be expected fluorene and cyclopentadiene exhibit the highest acidities of the hydrocarbons. In contrast to solution data, however, fluorene is a better acid in the gas phase than is cyclopentadiene. This result may be rationalized on the basis of the much higher degree of charge delocalization possible in the fluorenyl anion leading to a greater resonance stabilization. As discussed in section 7, in solution this extensive delocalization leads to weaker anion–solvent interactions and causes fluorene to be a weaker solution acid than cyclopentadiene.

As pointed out in the previous publication[5] Bohme's data[3] showed that the gas phase acidity of propylene is close to that of toluene and the present results showed that the acidity of 1,4-pentadiene is close to that of diphenylmethane which points to the fact that the stabilization by phenyl of vinyl groups is of similar magnitude. A closer look at the values brings out an additional interesting effect. Bohme's data[3] showed that in the gas phase propene is a weaker acid by about 3 kcal/mol than toluene.[3] On the basis of cumulative substituent effects it might then be expected that diphenylmethane would be a stronger acid than 1,4-pentadiene by between 3 and 5 kcal/mol. However, just the reverse is observed. It is found that 1,4-pentadiene is the stronger acid by about 1 kcal/mol. This result is likely an indication that the phenyl rings in the diphenylmethyl anion are slightly twisted out of the plane of the π system which reduces the amount of resonance stabilization relative to that possible in pentadienyl anion.[14]

4. Carbon Acids with Nitrile Substituents. The results obtained for gas phase acidities of cyano-substituted hydrocarbons are shown in Table II. The effect of adding a cyano group on acidity is dramatic. For example, a cyano group substituted in the α position of toluene increases the gas phase acidity by

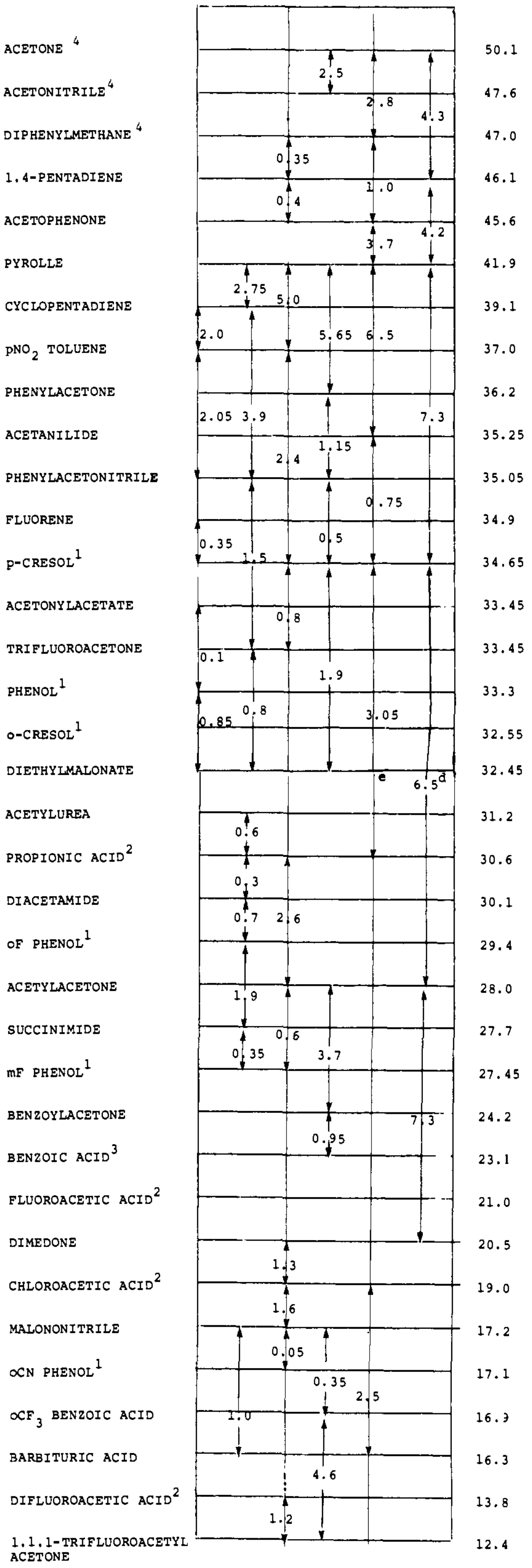
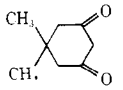


Figure 1. Summary of gas phase proton transfer equilibria measurements involving carbon and nitrogen acids. Numbers between double arrow give $\Delta G°$ for reaction $R_1H + R_2^- = R_1^- + R_2H$ at 600 °K in kcal/mol. Numbers in the column to the right give values for the difference between the bond dissociation energy and the electron affinity: D(R–H) − EA(R) in kcal/mol. Compounds arranged in order of decreasing D − EA, i.e., in order of increasing gas phase acidity. (1) Internal standards with superscript: 1 from ref 11. (2) From ref 7 and 9. (3) From ref 10. (4) The measurement of the above equilibria was more difficult than the measurements involving other acids. Therefore an error of ±1 kcal/mol may be present for these results. Bohme[3] has reported exothermic proton transfer from acetone to $CNCH_2^-$ which is in disagreement with the greater acidity of acetonitrile reported above.[27]

Table III. Carbonyl Acidities

Species	D(RH) − EA (R), kcal/mol	pK_a
1,1,1-Trifluoroacetylacetone $CF_3COCH_2COCH_3$	12.4	4.7
Barbituric acid	16.3	4
Dimedone 	20.5	5
Benzoylacetone $PhCOCH_2COCH_3$	24.2	9.4
Acetylacetone $CH_3COCH_2COCH_3$	28.0	9.0
Diethyl malonate $C_2H_5OCOCH_2CO_2C_2H_5$	32.45	13.3
1,1,1-Trifluoroacetone CF_3COCH_3	33.45	
Acetonyl acetate $CH_3COCH_2OCOCH_3$	33.45	
Phenylacetone $PhCH_2COCH_3$	36.2	
Acetophenone $PhCOCH_3$	45.6	19
Acetone CH_3COCH_3	50.4	20

more than 32 kcal/mol and a second cyano group added to acetonitrile increases acidity by about 30 kcal/mol (see Table I). This pronounced effect is a consequence of the effectiveness of the cyano group in stabilizing both radical and anionic centers by resonance interactions.

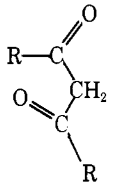
A comparison of the relative gas phase and solution acidities of cyano-substituted hydrocarbons and some common oxygen acids reveals that the cyano-substituent effect is much more pronounced in the gas phase. Thus while acetonitrile is 9 pK_a units weaker in acidity than methanol in solution its gas phase acidity is roughly 24 kcal/mol greater. Similarly, a comparison of malonitrile with a strong carboxylic acid chloroacetic acid shows that even though chloroacetic acid is 8 pK_a units stronger in solution it is 1.8 kcal/mol weaker than malononitrile in the gas phase. This reversal is again likely due to lower energy solvation interactions of solvent with charge delocalized anions (see also section 7).

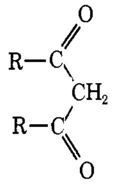
The present observation that acetonitrile is a stronger acid than acetone (Table I) is not in agreement with Bohme's[3] gas phase acidities which show a reversed order. As discussed in section 8 an interference by a side reaction was encountered in the present measurement. This reduces somewhat the confidence in the present result. Experiments are presently in progress in our laboratory with the intent of clearing up this discrepancy.[27]

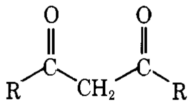
5. Carbonyl Acidities. The gas phase acidities of a number of mono and dicarbonyl compounds are listed in Table III in order of decreasing acidity. Inspection of the table shows a qualitative correlation with the solution acidities which decrease on the whole in the same order.

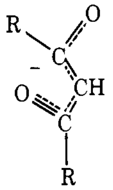
It should be noted that in solution the monoketo compounds are generally in the keto form while the diketo compounds are mostly in the enol form.[15] The major factor causing the higher stability of the enol form in the diketo compounds is the stabilization of the enol by the internal hydrogen bond formed to the other oxygen atom.[15] In the gas phase and at low (room) temperature this stabilization should be even more important. However, since the internal hydrogen bond is formed with the loss of a few to several entropy units,[15] we expect that in the gas phase at 327 °C the diketo compounds will be completely in the keto form. The general correlation of the gas phase and solution acidities occurs in spite of the presence of either the enol form (diketo compounds) in solution and the keto form in the gas phase since the keto-enol stability differences in solution are small compared to the electronic effects introduced by the substituent changes from compound to compound.

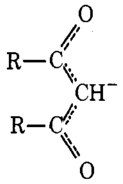
At first glance it seems surprising that dimedone should be nearly 8 kcal/mol more acidic than acetylacetone. However, this difference may be rationalized on the basis of conformation of the respective anions. There are three possible stable conformations of β-dicarbonyl neutrals, I, II, III, and anions, Ia, IIa, IIIa.[16] For small R groups such as methyl, configurations

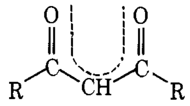

I


II


III


Ia


IIa

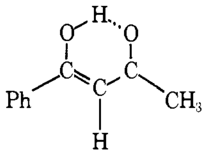

IIIa

such as I and II are most probably due to a minimization of dipole-dipole repulsions. However, for larger R groups steric repulsions make configurations I and II highly unlikely and III is the most probable form. Thus for acetylacetone it seems likely that the neutral molecule takes a form similar to I or II with possibly a small amount of twisting out of the plane to reduce steric hindrance of the methyl groups. Similar arguments apply in the anion with the added effect that forms such as IIIa are made more unfavorable by the close interaction of the negatively charged oxygens. Thus the acetonylacetone anion also is in a form much like Ia or IIa twisted slightly out of a planar form. It is this nonplanarity of the anion which should account for the lower acidity of acetylacetone relative to dimedone. The nonplanarity of the π-electron system inhibits the resonance delocalization of charge and reduces the amount of stabilization relative to that possible in a planar π arrangement. In contrast in dimedone the cyclic nature of the anion forces the π system to be planar with a C-C-C bond angle of 120° which is ideal for overlaps with the sp^2 hybridization of the central carbon. In addition the oxygens are forced to be far apart reducing repulsive charge interactions. The complete resonance stabilization and favorable geometry in the dimedone anion thus result in a net increase in stability of 8 kcal/mol over that in acetylacetone.

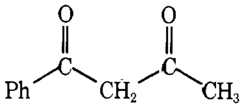
A comparison of the acidities of acetone and acetonyl acetate reveals the effectiveness of the carboxyl group, RCO_2, in increasing C-H acidity. In acetonyl acetate anion conjugation of negative charge with only one carbonyl group is possible yet it is still 17 kcal/mol more acidic than acetone. This extra 17 kcal/mol is a result of the effectiveness of the carboxyl group in stabilizing negative charge by inductive effects and in lowering the C-H homolytic bond dissociation energy.

The effect of the trifluoromethyl group in inductively stabilizing negative charge is shown in comparisons of the acidities of acetylacetone with 1,1,1-trifluoroacetylacetone and acetone with 1,1,1-trifluoroacetone. In each case the increase in acidity is roughly 16 kcal/mol which is comparable to the effect of a substituent which is able to stabilize negative charge by charge delocalization. This effect is also evident[11] in a dramatic increase in benzoic acid and phenol acidities with trifluoromethyl substitution.

In comparing the relative gas phase and solution acidities of acetylacetone with benzoylacetone a consideration of keto-enol tautomerism becomes important. It has been observed in the neat liquids at 35 °C that acetylacetone and benzoylacetone are 78 and 9 enolized respectively and in solution have pK_a values of 9.0 and 9.4.[15] This is the reverse of the order of acidities that might have been expected in solution since benzoic acid is observed to have a pK_a of 4.2 while that of acetic acid is 4.75. This reversal of acidity order is almost certainly due to stabilization of the free acid by enolization in benzoylacetone. In order to minimize steric effects it is likely that benzoylacetone enol has the form IV which allows it to be stabilized by an internal hydrogen bond. In the gas phase and at high temperature it is likely that benzoylacetone will revert predominantly to the keto form, V, although for steric reasons it will maintain much the same geometry as the enol (IV). As a result the more "normal" order of substituent effects is observed in the gas phase with benzoylacetone being more acidic by 3.8 kcal/mol than acetylacetone. This is very similar to the 5-kcal/mol difference observed between acetophenone and acetone.



IV



V

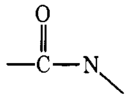
6. Nitrogen Acids. The gas phase acidities of the nitrogen acids studied are listed in Table IV. These compounds are rarely thought of as being acidic species and in fact it was possible to find a reported pK_a value for succinimide only.

It is of interest to compare the gas phase acidities of analogous nitrogen and carbon acids. It is known that the N-H bond strength in ammonia is 110 kcal/mol and that for methane 104 kcal/mol. However, Bohme et al.[3] have determined that the acidity of methane is less than that of ammonia by virtue of failure to observe the reaction

$$\mathrm{NH_2^- + CH_4 \nrightarrow NH_3 + CH_3^-} \qquad (10)$$

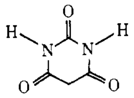
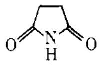
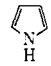
This and the higher electronegativity of nitrogen relative to carbon would indicate that we can expect nitrogen compounds to be better acids than the analogous carbon compounds. However, this is not always the case as seen by the fact that diacetamide is 2 kcal/mol weaker than acetylacetone and pyrrole is nearly 3 kcal/mol weaker than cyclopentadiene. Acetanilide, on the other hand, obeys our predicted result being 1 kcal/mol stronger than phenylacetone. This ambiguity in carbon and nitrogen acidities may be explained by the ability of nitrogen compounds to be stabilized by delocalization of the nitrogen atom lone pair as shown in the resonance forms VI, VII, and VIII. The stabilization of the neutral molecule, which is not possible in analogous carbon compounds, is comparable to the stabilization of nitrogen free radicals and hence the N-H bond strength is not lowered to the same extent by substituents as it is in carbon compounds. Only in the case of acetanilide is there a sufficient weakening of the N-H bond strength by phenyl substitution to observe the acidity order predicted from ammonia-methane results. The order of substituent effects in increasing N-H acidity is thus acetyl > phenyl > vinyl.

On the basis of the greater acidity of acetylacetone relative to diacetamide it is possible to conclude that the C-H bond is more acidic than the N-H bond of barbituric acid (IX). The acidity of barbituric acid is about 4 kcal/mol greater than dimedone implying that the negative charge is stabilized by the inductive effect of the

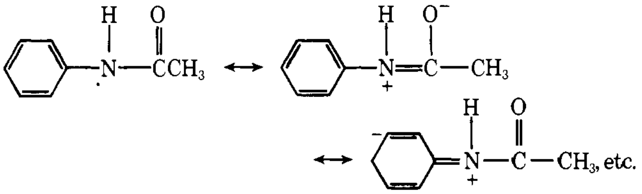


group. The higher acidity of the C-H bond in barbituric acid may also be the reason explaining the observation that 5,5′-diethylbarbituric acid (barbital) (X) is 4 pK_a units weaker than the unsubstituted barbituric acid in solution.

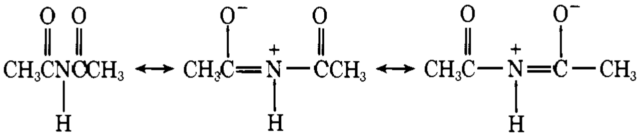
Table IV. Nitrogen Acids

Species	D(RH) − EA(R), kcal/mol	pK_a
Barbituric acid[a] 	16.3	4
Succinimide 	27.7	10.5
Diacetamide $CH_3CONHCOCH_3$	30.1	
Acetylurea $CH_3CONHCONH_2$	31.2	
Acetanilide $PhNHCOCH_3$	35.3	
Pyrrole 	41.9	

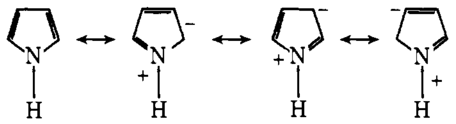
[a] According to discussion presented in the text, barbituric acid is not a nitrogen but a carbon acid, since the C-H protons are more acidic.



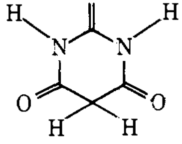
VI



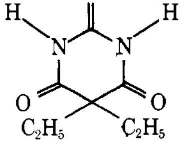
VII



VIII



IX



X

7. General Comparison with Solution Acidities. From a general comparison of solution and gas phase acidities, information regarding the factors governing solvation and solvation energies may be obtained. For example, in comparing a number of carbon acids to methanol it is found that although in solution acetone, acetonitrile, diphenylmethane, and acetophenone are 4, 9, 19, and 3 pK_a units weaker than methanol respectively in the gas phase they are 21, 23, 24, and 25 kcal/mol stronger. This reversal should largely be accounted for by the differences in solvation of the methoxide ion and the various substituted carbanions. In the methoxide ion the negative charge is mostly localized on the oxygen atom, with a slight amount of negative charge on the methyl group due to inductive and polarization interactions. On the other hand, in the four carbon acids considered above the negative charge is delocalized by resonance to varying degrees. The reason for correlation of charge delocalization and solvation energy may be qualitatively understood by consideration of the Born equation. The free energy of solvation of a single ion is given by the Born equation (eq 11),[17] where z is the fractional

$$\Delta G_{\text{solv}} = \frac{z^2e^2}{2r}\left(1 - \frac{1}{\epsilon}\right) \tag{11}$$

charge, e the unit electronic charge, r the ion radius, and ϵ the dielectric constant of the medium. For negative ions such as the halide ions and alkoxide ions z^- on the O atom is not far from unity. However, in an anion where charge is significantly delocalized the total solvation energy may be considered as a sum of solvation energies of each of the fractional charge centers of the ion. For example, if we compare the solvation energy of one unit of negative charge localized on a single atom with the solvation energy of one unit of negative charge delocalized uniformly over n identical centers, the ratio of solvation energies may be roughly estimated by eq 12. This equation is

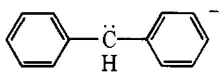
$$\frac{\Delta G_1}{\Delta G_2} = \frac{n(z_1)^2}{z_2^2} = \frac{n(1/n)^2}{1} = \frac{1}{n} \tag{12}$$

obtained by assuming that the charge localized ion and the charge centers of the delocalized ion each have the same radius. Thus the solvation energy of a particular ion will decrease approximately in proportion to the number of centers over which charge is delocalized.

Since all four of the carbon acids considered above have roughly equal gas phase acidities, from the order of solution acidities it can be seen that the order of solvation energies of the anions is acetophenone ≈ acetone > acetonitrile > diphenylmethane. From the argument above based on the Born equation for solvation energies diphenylmethane is definitely expected to have the lowest solvation energy since it has the greatest charge delocalization. The charge distribution in the diphenylmethyl anion determined from NMR experiments[18] is shown in Table V. Assuming that the negative charge of the methoxide ion is localized on the oxygen, while it is delocalized as in Table V for the diphenylmethyl anion, one can calculate from eq 11 and 12 that the energy of solvation of the diphenylmethyl anion is only about one-tenth of that for the methoxide. Since solvation energies for large uninegative ions are typically in the range 50–100 kcal/mol it is easy to see that the difference in solvation energies can easily overwhelm and reverse the intrinsic gas phase acidity difference of 24 kcal/mol of the two molecules.

It should be pointed out that eq 12 is a rough approximation and similar approximations could be obtained from the alternate approach of assuming that the charge is evenly distributed over the whole (charge delocalized) molecule leaving $z = 1$ (eq 11) and selecting a radius that would give a spherical volume equal to the molecular volume. In such a calculation the decrease of solvation energy will appear as due to an increase of volume of the ion. This of course is also a valid qualitative standpoint since expansion of the conjugated system leads to both increase of delocalization and of volume.

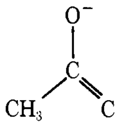
Table V. Charge Distribution in Diphenylmethyl Anion[b]



Position	Charge[a]	No. of positions	Total charge[a]
Ortho	−0.08	4	−0.32
Meta	−0.07	4	−0.28
Para	−0.16	2	−0.32
Methyl	−0.08	1	−0.08

[a] In units of charge of an electron. Charge distributions measured in THF solution. [b] Taken from ref 18.

From the observation that the acetonyl anion is better solvated than the cyanomethyl anion some inferences concerning the charge distributions in these two anions may be made. Since each anion can have charge delocalized on only two centers it must be that in the cyanomethyl anion the charge is more evenly distributed between carbon and nitrogen leading to a lower solvation energy. In the acetonyl anion one center will bear a greater fraction of the charge and thus it seems likely that the anion will be predominantly in the form XI which leads to favorable solvation.



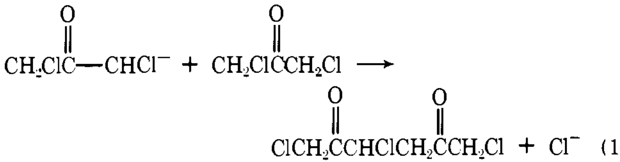
XI

8. Nucleophilic Displacement Reactions. In addition to the compounds already mentioned in this paper a number of others were investigated which should have been appreciably acidic in the gas phase. For example, according to the data of Bohme et al. nitromethane should be slightly more acidic than cyclopentadiene.[3] However, all attempts to obtain equilibrium of nitromethane with other species were unsuccessful since the intensity of the nitromethyl anion decayed faster than the anion of the reference acid. In addition an attendant increase in intensity of NO_2^- was observed leading us to suspect that the nucleophilic displacement reaction 13 was taking place. The

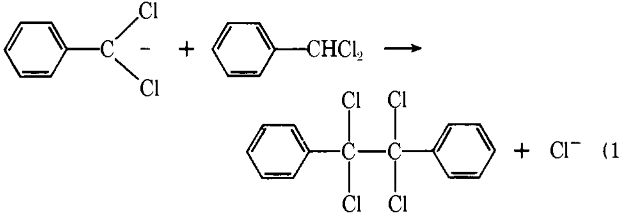
$$CH_2NO_2^- + CH_3NO_2 \longrightarrow CH_3CH_2NO_2 + NO_2^- \tag{13}$$

observation of an increase in the rate of decay of $CH_2NO_2^-$ with increasing CH_3NO_2 pressure presented further evidence for this reaction.

Similar reactions were observed for a number of systems which possess good leaving groups such as Cl^- as illustrated in reactions 14 and 15 below for 1,3-dichloroacetone and benzalchloride, respectively.



$$CH_2Cl\overset{\text{O}}{\overset{\|}{C}}{-}CHCl^- + CH_2Cl\overset{\text{O}}{\overset{\|}{C}}CH_2Cl \longrightarrow ClCH_2\overset{\text{O}}{\overset{\|}{C}}CHClCH_2\overset{\text{O}}{\overset{\|}{C}}CH_2Cl + Cl^- \tag{14}$$



(15)

In addition to these reactions it was expected that reaction 16 for acetonitrile should be exothermic. Consequently it was

$$CH_2CN^- + CH_3CN \longrightarrow CH_3CH_2CN + CN^- \tag{16}$$

possible to obtain an equilibrium between acetonitrile and acetone only by keeping the concentration of acetonitrile very low such that proton transfer could occur much faster than nucleophilic displacement.

Bohme has reported that reaction 16 is not observed at 298 K in a flowing afterglow apparatus.[3] However, in view of recent observations of activation energies for nucleophilic displacement reactions[19,20] it is reasonable to assume that if the activation energy for reaction 16 is greater than 5 kcal/mol it would not be observed at 298 K but would proceed readily at 600 K in our apparatus.

9. Thermochemistry. As shown in eq 3 a determination of the absolute gas phase acidity of a molecule RH may be directly related to the difference in homolytic bond dissociation energy, D(R–H), and the radical electron affinity, EA(R). If either of these quantities is known the other may be automatically obtained from the gas phase acidity. In addition cases where both the bond energy and radical electron affinity are known provide a check on the accuracy of our absolute acidity scale developed from multiple thermodynamic cycles and use of HCl and H_2S as standard reference points. For example, the gas phase acidity of cyclopentadiene may be calculated from the C–H bond energy determined by Benson[21] (81.2 kcal/mol) and the electron affinity of the cyclopentadienyl radical obtained by Brauman[22] (42.4 kcal/mol). The value of acidity obtained from these thermochemical data is 38.8 kcal/mol. This is in excellent agreement with the value determined here by us, 39.1 kcal/mol, and provides one further check on the accuracy of our absolute acidity scale.

Unfortunately thermochemical data for the pertinent bond energies or electron affinities are very scarce. However, in many cases it is possible to make reasonable estimates of bond energies on inferences from known data and to obtain electron affinities of a number of organic radicals to within a few kilocalories per mole. The method of obtaining electron affinities from bond dissociation energies and gas phase acidities has the advantage that all anions and neutrals are thermalized in contrast to photodetachment and other direct EA determinations where often nonthermal species are involved. The values of electron affinities together with the value of acidities and the estimated bond energies are summarized in Table VI.

The assignment of C–H bond energies in β-dicarbonyl compounds is based on Benson's observation that in acetone the carbonyl group provides no resonance stabilization to the acetonyl radical.[23] Thus it appears logical that since the C–H bond energies in acetone and ethane are the same then the C–H bond energy in β-dicarbonyl compounds should be the same as the $(CH_3)_2CH$–H bond energy in propane, 94.5 kcal/mol.[13] Similarly, in the mono carbonyl compounds the C–H bond energy is assumed to be equal to that in acetone. Phenylacetone is the exception where the C–H bond energy is assigned a value of 83 kcal/mol. This is 3 kcal/mol smaller than the $PhCH_2$–M bond energy in toluene, 85 kcal/mol,[13] and takes into account the fact that a secondary hydrogen is involved. The C–H bond energy in acetonylacetate is assigned as 88 kcal/mol on the basis of the observation that the bond energy CH_3OCH_2–H is 94 kcal/mol, 10 kcal/mol less than CH_3–H. Thus the C–H bond energy in acetonyl acetate should be 10 kcal/mol less than that of acetone.

Some data exist for each of the hydrocarbons except fluorene. For fluorene it is assumed that the C–H bond energy will be 1 kcal/mol less than that in cyclopentadiene. The benzylic C–H bond energy in p-NO_2PhCH_3 is assumed the same as that in toluene on the basis of studies of thermal decomposition of substituted benzyl bromides in which it was found that the C–Br bond strength did not change with substitution in the ring.

Assumptions for the C–H bond strengths in malononitrile and phenylacetonitrile are based on the observation that propene, toluene, and acetonitrile all have similar bond energies.[13] Thus if phenyl, vinyl, and cyano groups have nearly equal effects on stability of radicals then phenylacetonitrile and malononitrile should have C–H bond energies similar to 1,4-pentadiene and diphenylmethane.

Table VI. Summary of Thermochemical Data

Species	D(RH) – EA (R),[a] kcal/mol	D(R–H), kcal/mol	EA(R), kcal/mol
Fluorene	34.9	80 ± 5[b]	45 ± 5[c]
Cyclopentadiene	39.1	81.2 ± 1.2[d]	42.4 ± 0.7[e] 42.15[f]
1,4-Pentadiene	46.1 ± 0.4	68.5 ± 3[g]	22.4 ± 3[h]
$PhCH_2Ph$	47.0 ± 0.4	66 ± 6[i]	19 ± 6[f]
$CH_2(CN)_2$	17.2	70 ± 5[b]	53 ± 5[c]
$PhCH_2CN$	35.1	70 ± 5[b]	45 ± 5[c]
CH_3CN[27]	47.9 ± 0.4	82.3 ± 3[b]	34.7 ± 4[c]
$PhCH_3$	37.0	85 ± 5[b]	48 ± 5[c]
$CF_3COH_2COCH_3$	12.4	94 ± 5[b]	82 ± 5[c]
Dimedone	20.5	94 ± 5[b]	73.5 ± 5[a]
$PhCOCH_2COCH_3$	24.2	94 ± 5[b]	70 ± 5[c]
$CH_3COCH_2COCH_3$	28.0	94 ± 5[b]	66 ± 5[c]
CF_3COCH_3	33.5	98 ± 3[b]	64.5 ± 3[c]
$PhCH_2COCH_3$	36.2	85 ± 5[b]	49 ± 5[c]
$PhCOCH_3$	45.6	98 ± 3[b]	52.4 ± 4[c]
CH_3COCH_3	50.4 ± 0.4	98 ± 3[j]	47.6 ± 4[f]
$CH_2(CO_2C_2H_5)_2$	32.5	94 ± 5[b]	61.5 ± 5[c]
CH_3COCH_2OCO-C_2H_5	33.5	88 ± 5[b]	52.5 ± 5[c]
Succinimide	27.7	103 ± 5[k]	75 ± 5[f]
$CH_3CONHCOCH_3$	30.1	103 ± 5[b]	73 ± 5[c]
$PhNHCOCH_3$	35.3	80 ± 5[b]	45 ± 5[c]

[a] Determined in this work. All values ±0.2 kcal/mol unless otherwise indicated. [b] Authors' estimate. See text. [c] Obtained using the difference in measured value of acidity and estimated bond energy. [d] S. Furuyama, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.* 3, 237 (1971). [e] J. H. Richardson, L. M. Stephenson, and J. I. Braumann, *J. Chem. Phys.*, 59, 5068 (1973). [f] Obtained using the difference in measured value of acidity and literature value of bond energy. [g] Obtained using the difference in measured value of acidity and theoretical calculation value for electron affinity. [h] J. R. Hoyland and L. Goodman, *J. Chem. Phys.*, 36, 21 (1962). [i] S. W. Benson and H. E. O'Neil, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 21 (1970). [j] R. K. Solly, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, 2, 11 (1970). [k] Reference 26.

Nitrogen acids and N–H bonds are the group for which the least thermo-chemical data exist. Hedaya[26] has assigned a value of 100 kcal/mol for the N–H bond energy in succinimide from studies of decomposition of carbamates, RCO_2O-t-Bu, in which it was found that the rate of decomposition is slower for R = succinimide than R = NH_2. This result implies that the succinimidyl radical is less stable than NH_2 and allows an estimate of 103 ± 5 kcal/mol to be made for the N–H bond strength. Since it appears that carbonyl groups then give no significant stabilization to nitrogen radicals, diacetamide is also assigned a value of 103 ± 5 kcal/mol for the N–H bond energy. Analogously to phenylacetone the N–H bond energy in acetanilide is assumed similar to that in aniline, 80 kcal/mol.[13] Lack of any data for vinylamine M–H bond energies made an assignment of the pyrrole N–H bond energy impossible.

Even though many of the electron affinities listed in Table VI are based on somewhat rough estimates they still should be a useful addition to the very limited number of organic free radical electron affinities which have been determined to date. Using electron affinity as a measure of anionic stability it may be seen that some carbanions and nitrogen anions are as stable negative ions as the halide ions. From the derived values it may be seen that of analogous nitrogen and carbon radicals the nitrogen species will usually have the higher electron affinity. The order in which substituents are found to stabilize negative charge in carbanions is found to be $CF_3CO > PhCO > CH_3CO > CN$ vinyl ≈ phenyl. In special cases such as the cyclopentadienyl anion and fluorenyl anion special stability results from the aromatic character of the anion. In addition in the case of β-dicarbonyl compounds cyclization enhances the anion stability as in dimedone by constraining the π system to a planar geometry which allows maximum charge delocalization.

References and Notes

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(27) NOTE ADDED IN PROOF. Measurements just completed by M. French in our laboratory show that the measurement of the equilibrium $CH_3COCH_3 + CNCH_2^- = CH_3COCH_2^- + CH_3CN$ leads to $\Delta G^\circ = -2.6$ and not $+2.5$ kcal/mol as shown in Figure 1. This leaves $D - EA$ for acetone unchanged but gives for acetonitrile 52.7 kcal/mol (see Figure 1). This value leads to 29.6 kcal/mol for the EA of CH_2CN (see Table VI).

Long-Range Carbon–Carbon Spin–Spin Coupling Constants in Carboxyl Labeled Aromatic Carboxylic Acids and Dihydro Aromatic Carboxylic Acids

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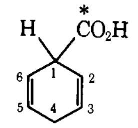
Abstract: The following compounds, both natural and labeled in the carboxyl position with >90% ^{13}C, were synthesized and studied by carbon NMR to obtain carbon chemical shifts and all carbon–carbon coupling constants involving the labeled carboxyl carbon: 1,4-dihydrobenzoic acid (**1**), 1,4-dihydro-1-naphthoic acid (**2**), 9,10-dihydro-9-anthroic acid (**3**), benzoic acid (**4**), 1-naphthoic acid (**5**), and 9-anthroic acid (**6**). Chemical shift assignments for **1–6** were aided by the chemical shifts for the parent hydrocarbons **7–9**, generated in this study. A breakdown of the expected dihedral angular dependence of the three-bonded carbon–carbon coupling constants is experienced in the series **1–3**, and for a conformational analysis of this series, an analysis of longer-range couplings is necessary. These longer-range couplings appear to arise from an additional π contribution as the $C-CO_2H$ carbon–carbon bond becomes more nearly parallel to the aromatic p orbitals of **2** and **3**. Such longer-range couplings are not observed for the fully aromatic compounds **4–6**, even though a completely conjugated coupling route is available. This conformational analysis of the series **1–3** indicates that the degree of puckering in **2** is intermediate between that in **1** and that in **3**.

In this paper experimental and theoretical studies of $^{13}C-^{13}C$ coupling are extended to two classes of compounds: 1,4-dihydro aromatic carboxylic acids (**1–3**) and aromatic carboxylic acids (**4–6**). This has been accomplished by the synthesis and carbon NMR spectroscopic studies of carboxyl labeled **1–6**. It is shown that the data generated thereby overcome certain inadequacies which were previously encountered in the use of proton–proton coupling constants in the conformational analysis of **1–3**.[2] Further, some rather interesting trends in the coupling constants of **4–6**, the synthetic precursors to **1–3**, are noted.



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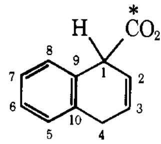

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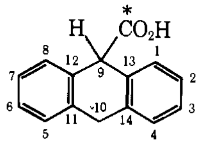

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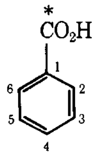

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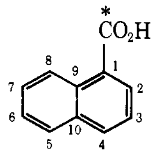

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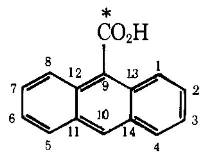

6

The vicinal $^{13}C-^{13}C$ coupling constants in aliphatic and alicyclic organic compounds have been shown to be related to dihedral angle,[3] and it was anticipated that a similar relationship would be followed in the series of compounds studied here. For example, **1** is known to be flat[4] and **3** is known to be puckered,[5] so that the experimental values of $^3J_{cc}$ of **2** would be indicative of the extent of puckering of the dihydro ring.

As this study developed, it became apparent that the $^3J_{CC}$ couplings in **1–3** do not obey the expected dependence on dihedral angle. However, long-range couplings were observed in **2** and **3** which were absent in the fully aromatic compounds