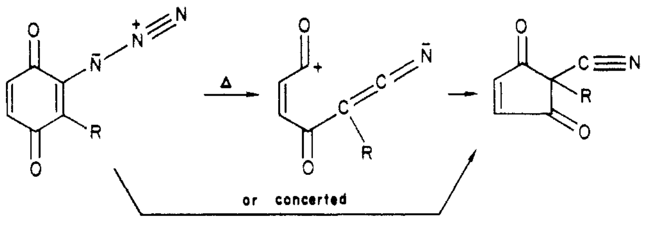
Scheme I



Scheme II

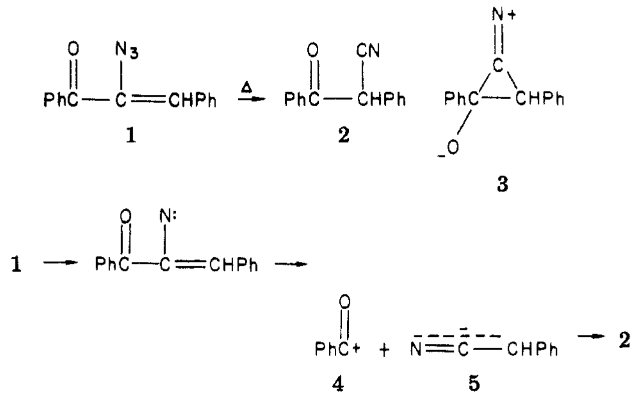
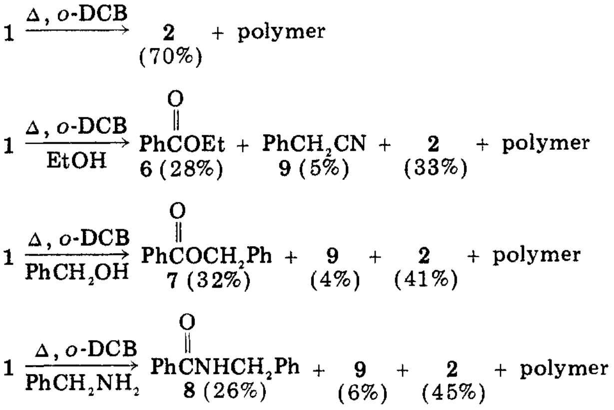


Table I. Trapping of Intermediates in the Thermolysis of 1 in *o*-Dichlorobenzene (*o*-DCB)



$$1 \xrightarrow{\Delta,\ o\text{-DCB}} \underset{(70\%)}{2} + \text{polymer}$$

$$1 \xrightarrow[\text{EtOH}]{\Delta,\ o\text{-DCB}} \underset{6\ (28\%)}{\text{Ph}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{OEt}} + \underset{9\ (5\%)}{\text{PhCH}_2\text{CN}} + \underset{(33\%)}{2} + \text{polymer}$$

$$1 \xrightarrow[\text{PhCH}_2\text{OH}]{\Delta,\ o\text{-DCB}} \underset{7\ (32\%)}{\text{Ph}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{OCH}_2\text{Ph}} + \underset{(4\%)}{9} + \underset{(41\%)}{2} + \text{polymer}$$

$$1 \xrightarrow[\text{PhCH}_2\text{NH}_2]{\Delta,\ o\text{-DCB}} \underset{8\ (26\%)}{\text{Ph}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{NHCH}_2\text{Ph}} + \underset{(6\%)}{9} + \underset{(45\%)}{2} + \text{polymer}$$

These results lend support to the generality of the zwittazido cleavage as a stepwise process.

Experimental Section

General. α-Azidochalcone (1), mp 63–64 °C, was prepared by the method of L'abbé and Hassner (lit.[5] mp 63.5–64 °C). The solvents, alcohols, and amine were distilled before use.

The esters, nitriles, and amide were identified by comparison of melting and boiling points, and nuclear magnetic resonance and infrared spectra with authentic samples.

Trapping of Intermediates in Thermolysis of α-Azidochalcone. General Procedure. To a solution of 2.49 g (10 mmol) of α-azidochalcone in 25 mL of *o*-dichlorobenzene was added 100 mmol of alcohol or amine. The magnetically stirred solution was then heated to reflux. When N_2 evolution ceased, the solvent was removed by low-pressure distillation to leave the crude product mixture.

The products were further separated and purified by distillation for liquids and crystallization for solids.

Acknowledgment. This research was supported by PHS Grant CA19203 from the National Cancer Institute.

Registry No. 1, 26087-01-4; 2, 5415-07-6; 6, 93-89-0; 7, 120-51-4; 8, 1485-70-7; 9, 140-29-4.

Acidities of Carbon and Nitrogen Acids: The Aromaticity of the Cyclopentadienyl Anion

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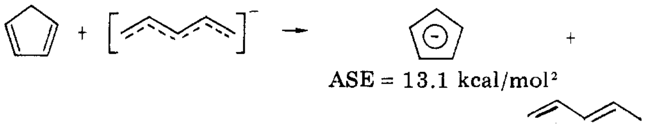
It is generally agreed that the relatively high acidity of 1,3-cyclopentadiene (CPH) is due primarily to aromatic stabilization of the cyclopentadienyl anion (CP^-), but there is little information available as to the size of this aromaticity effect. By use of the simple Hückel theory the π stabilization energy of the cyclopentadienyl anion is calculated to be 2.47β,[1] i.e., greater than that of benzene (2β); but the simple Hückel theory is known to exaggerate the aromatic stabilization energies.[1b] Adopting $\beta = 18$ kcal/mol, based on the empirical resonance energy of 36 kcal/mol, derived from the heat of hydrogenation of benzene relative to cyclohexene, places the resonance energy of CP^- at 57 kcal/mol. On the other hand, the aromatic stabilization energy (ASE) of CP^- is calculated to be only 13 kcal/mol, as compared to 25.6 kcal/mol for benzene, based on the heat of formation of benzene and that calculated by using MINDO/3 for the reaction of CP with the anion derived from (*E*)-1,3-pentadiene.[2]


ASE = 13.1 kcal/mol[2]

To these calculated resonance energies we now add several experimentally based estimates. Our estimates, derived from equilibrium acidity data in dimethyl sulfoxide solution,[3] indicate that the aromatic stabilization energy of CP^- is about 24–27 kcal/mol.

Results and Discussion

Aromatic Stabilization Energies of 1,3-Cyclopentadiene, Indene, and Fluorene Anions Determined by Comparison with Nitrogen Analogues. The equilibrium acidities in Me_2SO of 1,3-cyclopentadiene (CPH), indene (INH), and fluorene (FLH) decrease in that order, whereas the acidities of their nitrogen acid analogues, pyrrole, indole, and carbazole, are in the reverse order (Table I). The small increases in acidity of indole and carbazole, relative to pyrrole, can be attributed to small increases in inductive and/or resonance effects resulting from the presence of the additional benzene ring(s). The successive decrease in acidities of CPH, INH, and FLH can be attributed to successive decreases in the aromaticities of the CP^-, IN^-, and FL^- anions, which overshadow the acidifying effects of the benzene ring(s). The decreasing aromaticities are analogous to those observed (per benzene ring) in the series benzene, naphthalene, and anthracene.[4]

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(1) (a) Roberts, J. D.; Streitwieser, A., Jr.; Regan, C. M. *J. Am. Chem. Soc.* **1952**, *74*, 4579–4582. (b) Ritchie, C. D. "Physical Organic Chemistry"; Marcel Dekker: New York, 1975; Chapter 5.

(2) Dewar, M. J. S. *Pure Appl. Chem.* **1975**, *44*, 767–782. The author suggests that this value may be too small since MINDO/3 tends to underestimate resonance energies of anions.

(3) Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006–7014.

Table I. Equilibrium Acidities in Dimethyl Sulfoxide Solution[a]

acid (HA)	InH[b]	pK_a (HIn)	pK_a (HA)	selected pK_a
1,3-cyclopentadiene	CNAH	18.90	17.94 ± 0.005	
	PFH	17.90	18.05 ± 0.038	18.0[c]
indene	CNAH	18.90	20.11 ± 0.015	
	2NPANH	20.66	20.13 ± 0.019	20.1[d]
fluorene				22.6[a]
pyrrole	FH	22.60	23.05 ± 0.007	
	MFH	22.34	23.05 ± 0.03	23.05
indole	2NPANH	20.66	20.90 ± 0.009	
	MFH	22.34	20.98 ± 0.02	20.95
carbazole	CNAH	18.9	19.87 ± 0.004	
	2NPANH	20.66	19.97	19.9

[a] See ref 3 and 14 for descriptions of the experimental methods used in carrying out these measurements. [b] Indicator (InH) abreviations are as follows: CNAH, 4-chloro-2-nitroaniline; PFH, 9-phenylfluorene; 2NPANH, 2-naphthylacetonitrile; FH, fluorene; MFH, 9-methylfluorene; TP2H, 1,3,3-triphenylpropene; T1200, benzyl methyl sulfone; T-BUFH, 9-*tert*-butylfluorene. [c] Earlier measurements by Matthews in Me_2SO gave a value of 18.1. [d] For a discussion of pK_a values in other media see: Bordwell, F. G.; Drucker, G. E. *J. Org. Chem.* **1980**, *45*, 3325-3328.

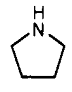
Table II. Equilibrium Acidities of Carbon Acids, GCH_3, and Nitrogen Acids, GNH_2, in Dimethyl Sulfoxide at 25 °C

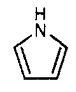
G	pK_a (GCH_3)	pK_a (GNH_2)	ΔpK_a
CN	31.3	17.0[b]	14.5
CH_3SO_2	31.1	17.5[b]	14
$PhSO_2$	29.0	16.1[b]	13
Ph	(42)[a]	30.7	11
			12[c]
H	(55)[a]	(41)[a]	14
			12[c]

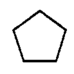
[a] Estimated from extrapolations; see text. [b] Algrim, D., unpublished results. [c] Gas phase (see ref 13).

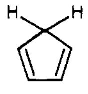
Nitrogen acids (N–H) have an intrinsically greater acidity than carbon acids (C–H) which is associated principally with the greater electronegativity of nitrogen than carbon. The difference in acidities in Me_2SO solution for nitrogen acids, GNH_2, and carbon acids, GCH_3, is about 14 pK_a units when G is CN, CH_3SO_2, or $PhSO_2$ (Table II), which is about the same as the difference we estimate for the solution acidities of NH_3 and CH_4, but slightly greater than the difference observed for the gas-phase acidities of NH_3 and CH_4 (Table II). The greater acidity of CPH than pyrrole by 5.3 pK_a units (Table I) represents a striking reversal of the relative intrinsic acidities of C–H and N–H acids. The extent of this reversal is about 19 pK_a units if pyrrole is assumed to have an intrinsically greater acidity than CP by 14 pK_a units. This corresponds to an aromatic stabilization energy (ASE) of the CP^- anion of about 26 kcal/mol. A similar reversal is observed for indene vs. indole, the latter being less acidic by 0.8 pK_a unit[5] which corresponds to an ASE of about 20 kcal/mol for the cyclopentadienyl moiety in the indenyl anion. Fluorene is less acidic than carbazole by 3.0 pK_a units.[5] Here the ASE of the cyclopentadienyl moiety is not large enough to make the stability of the fluorenyl anion overshadow the intrinsic stability of the carbazole anion; the ASE for the CP^- moiety in the fluorenyl anion is estimated to be about 14.5 kcal/mol.

The acidity of pyrrole relative to CPH can be used in another way to estimate the ASE of the CP^- anion. In this approach the acidity of pyrrole relative to that of its saturated analogue, pyrrolidine, is used as a model to assess the effect on acidity of introducing two C═C bonds α to the acidic site of cyclopentane. This structural change in pyrrolidine produces an aromatic molecule, pyrrole, whose conjugate base will not differ appreciably in aromaticity from that of the undissociated acid. On the other hand, the same structural change in cyclopentane will produce a nonaromatic molecule, 1,3-cyclopentadiene, whose conjugate base derives its stability to an appreciable extent from the "extra" delocalization provided by its closed shell 6π-electron structure.


p$K_a \simeq 44$


p$K_a = 23.0$


p$K_a \simeq 58$


p$K_a = 18.0$

The pK_a values shown for pyrrolidine and cyclopentane are approximate since they were estimated from extrapolations. An extrapolation from the acidities of malononitrile and acetonitrile can be used to estimate a minimum pK_a for methane of about 51.[6]

$$\begin{array}{ccccc} CH_2(CN)_2 & \xrightarrow{\Delta pK = 20} & CH_3CN & \xrightarrow{(+20)} & CH_4 \\ pK_a = 11.1 & & pK_a = 31.3 & & pK_a \simeq 51 \end{array}$$

This is a minimum value because it does not take into account the resonance saturation effect, which makes the acidifying effect of substitution of a second CN for H in methane smaller than the acidifying effect of the first. Assuming a saturation effect of the same size as that observed in the gas phase raises this value to 55.[6]

A similar method can be used to estimate the pK_a of toluene, using ΔpK_a = 20 for $CH_2(CN)_2$ vs. CH_3CN. (This estimate ignores differences in saturation effects for $PhCH_3$ and CH_3CN.)

$$\begin{array}{ccc} PhCH_2CN & \xrightarrow{(+20)} & PhCH_3 \\ pK_a = 21.9 & & pK_a \simeq 42 \end{array}$$

Extrapolations of this kind can be made with other functional groups, but CN has the advantage of smaller steric demands than most. The smaller acidifying effect and larger steric demand of phenyl prevent the direct use of this function in this manner, but acidities for toluene and for methane in the following series have been derived by other methods.

$$\begin{array}{ccccccc} Ph_3CH & \xrightarrow{\Delta pK = 1.8} & Ph_2CH_2 & \xrightarrow{\Delta pK \simeq 10} & PhCH_3 & \xrightarrow{\Delta pK \simeq 13} & \\ pK_a = 30.6 & & pK_a = 32.1 & & pK_a \simeq 42 & & \\ & & & & & & CH_4 \\ & & & & & & pK_a \simeq 55 \end{array}$$

A p$K_a \simeq 42$ for toluene can be estimated as described above and also from the intercept of a plot of the pK_a's of para-substituted anilines (p-$GC_6H_4NH_2$) vs. para-substituted toluenes (p-$GC_6H_4CH_3$) in Me_2SO (G = NO_2, F_3CSO_2, PhCO, $PhSO_2$, CN).[7,8]

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[4] Wheland, G. W. "Resonance in Organic Chemistry"; Wiley: New York, 1955; p 98. Swinborne-Sheldrake, R.; Herndon, W. C. *Tetrahedron Lett.* **1975**, 755–758.

[5] Statistically corrected for the difference in the number of protons and the difference in the symmetry of the anions, where pertinent.

[6] Algrim, D.; Bares, J. E.; Branca, J. C.; Bordwell, F. G. *J. Org. Chem.* **1978**, *43*, 5024–5026.

[7] Bordwell, F. G.; Algrim, D.; Vanier, N. R. *J. Org. Chem.* **1977**, *42*, 1817–1819.

[8] Other extrapolations have led to pK_a values for toluene in the range of 43–45; see: Bordwell, F. G.; Bares, J. E.; Bartmess, J. E.; Drucker, G. E.; Gerhold, J.; McCollum, G. J.; Van Der Puy, M.; Vanier, N. R.; Matthews, W. S. *J. Org. Chem.* **1977**, *42*, 326–332.

The $\Delta pK \simeq 13$ between toluene and methane was derived from a plot of α-Ph acidifying effects on a series of carbon acids, CH_3NO_2, $CH_2(CN)_2$, CH_3COCH_3, and CH_3CN, vs. the Hammett ρ values for the corresponding series of acids, $ArCH_2NO_2$, $ArCH(CN)_2$, $ArCH_2COCH_3$, and $ArCH_2CN$.[6] This α-Ph effect for methane of 13 was derived from the plot by using a ρ_m for $ArCH_3$ of 7.4 deduced by extension of ρ_m in the series $ArCH(CN)_2$ (ρ_m = 4.1), $ArCH_2CN$ (ρ_m = 5.5) to ρ_m = 7.4 for $ArCH_3$.[9]

To estimate a pK_a for cyclopentane we must assess the effect of replacement of two hydrogen atoms in methane by alkyl groups and the effect of incorporating these alkyl groups into a five-membered ring. Data in hand indicate that replacement of hydrogen by methyl in carbon acids forming relatively localized carbanions, such as in α-cyano or α-phenylsulfonyl carbanions, decreases the acidity by about 1 to 1.5 pK_a units.[11] This effect might be larger in the CH_3^- anion but should be reduced by the ring effect; a net increase of about 3 pK_a units for cyclopentane vs. methane therefore seems reasonable.

The pK_a of about 44 for pyrrolidine was derived by adding 3 pK_a units to the pK_a of ammonia following the reasoning given for approximating the difference between the pK_a's of cyclopentane and methane. Several methods have been used to estimate the pK_a of ammonia. One method is to start with the pK_a of cyanamide, H_2NCN, in Me_2SO and assume the same ΔpK_a as that between CH_3CN and CH_4 (24, when the saturation effect is included—see above).

$$\underset{pK_a = 17.0^{12}}{NH_2CN} \xrightarrow{\Delta pK_a = 24} \underset{pK_a \simeq 41}{NH_3}$$

Three other methods have been used to obtain extrapolated pK_a values for ammonia.[6] The average of the four values is 41.

The pyrrole anion is stabilized, relative to its saturated analogue, the pyrrolidinyl anion, by the presence of two α C=C bonds. The difference in the estimated solution pK_a of pyrrolidine (44) and the measured pK_a of pyrrole (Table I) is 21 pK_a units. Assuming that two α C=C bonds will stabilize the cyclopentyl anion by a like amount gives an estimated pK_a for 1,3-cyclopentadiene of 37 in the absence of aromaticity in the anion. The difference between this value and that observed (Table I) is 19 pK_a units, equivalent to about 27 kcal/mol in ASE. A similar estimate made from gas-phase data using the difference in acidities of ammonia and pyrrole relative to those of methane and 1,3-cyclopentadiene gives an ASE of about 23 kcal/mol.[13]

Aromatic Stabilization Energies of Cyclopentadienyl, Indenyl, and Fluorenyl Anions Based on Open-Chain Models. Another way to estimate ASE values for CP^-, IN^-, and FL^- anions is to compare the acidities of their conjugate acids with those of appropriate open-chain model compounds. For example, (*E*)-1,3-pentadiene, (*E*)-1-phenylpropene, and diphenylmethane can be used as models for CPH, INH, and FLH, respectively. The acidity of diphenylmethane has been measured in Me_2SO (pK_a = 32.1)[14] but the acidities of (*E*)-1,3-pentadiene and (*E*)-1-phenylpropene have not. There is reason to believe that the latter two will be less acidic than diphenylmethane since kinetic acidity data in Me_2SO suggests that an α-Ph group is more acidifying than an α-C=C group. Thus, the rate of isomerization in Me_2SO of 2-methyl-1-pentene catalyzed by *t*-BuOK is about 10 times the rate of deuterium exchange of 1-pentene under these conditions, and both of these rates are slower than the rate of isotopic exchange with toluene.[15] We note that the rate of isomerization of Me_2SO of 2-methyl-1-pentene catalyzed by CH_3SOCH_2K is 1.75 times *faster* than deuterium exchange with $C_6H_5CD_3$, under the same conditions.[16] But we can expect the rate for the alkene to be somewhat slower than that for toluene when the deuterium isotope effect is taken into account. Also, it is possible that the rate for toluene may be slowed more by internal return than that for 2-methyl-1-pentene.

The heat of reaction of excess CH_3SOCH_2K in Me_2SO with 1,4-pentadiene is $\Delta H_D = -8.03 \pm 0.4$ kcal/mol.[17] Judging from the report that the heat of isomerization of 1,4-pentadiene to (*E*)-1,3-pentadiene is −6.6 kcal/mol,[18] we conclude that most of the heat of reaction of 1,4-pentadiene with CH_3SOCH_2K is a heat of isomerization, and that very little deprotonation of (*E*)-1,3-pentadiene occurs under these conditions. It follows that the diene cannot be much more acidic than the solvent (pK_a = 35.1).[14] If we assume a pK_a of 35 for (*E*)-1,3-pentadiene, the aromatic stabilization energy for CP^- from this model is 17 pK_a units, equivalent to 24 kcal/mol. A similar estimate made from gas-phase data on 1,3-cyclopentadiene and (*E*)-1,3-pentadiene gives an ASE of 24.1 kcal/mol ($\Delta G°$; $\Delta H°$ = 23.1 kcal/mol).[20]

Fluorene is 9.5 pK_a units more acidic than diphenylmethane in Me_2SO. This is equivalent to about 13 kcal/mol in ASE (13.6 kcal/mol in the gas phase).[13] This figure is low, however, since it fails to take into account the resonance energy present in the fluorene molecule itself arising from the enforced coplanarity of the benzene rings. The correction will amount to at least 5–6 kcal/mol, judging from the 5–6-kcal/mol greater resonance energy of fluorene than biphenyl calculated from heats of combustion.[4] On the other hand, the estimated ASE will be high to the degree that the lack of coplanarity of the benzene rings in the Ph_2CH^- inhibits overlap with the p orbital in this carbanion. In any event, the comparisons of acidities in Me_2SO and the gas phase with open-chain models both suggest an order of aromatic stabilization energies $CP^- > IN^- > Fl^-$.

Summary and Conclusions. The difference in acidities between GCH_3 and GNH_2 for G = CN, $MeSO_2$, and $PhSO_2$ (ΔpK_a in Table II) is used to define the intrinsic acidities between carbon and nitrogen acids in Me_2SO solution. On the basis of this definition cyclopentadiene

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[9] A ρ of about 12 was estimated earlier from ρ_m for $ArNH_2$ and the slope of a plot of pK_a's of p-$GC_6H_4NH_2$ vs. p-$GC_6H_4CH_3$, where G = NO_2, F_3CSO_2, PhCO, $PHSO_2$, and CN. Recent work has shown, however, that in the $ArCH_2Ph$ and $ArCHPh_2$ series the σ_p^- values for NO_2 and PhCO are greatly exaggerated for these carbon acids, relative to those for the anilines.[10] For that reason it is inappropriate to use the slope of this line to calculate ρ_m for $ArCH_3$.

(10) Bares, J. E.; Twyman, C. L., unpublished results.

(11) Bordwell, F. G.; Bartmess, J. E.; Hautala, J. A. *J. Org. Chem.* **1978**, *43*, 3095–3101.

(12) Algrim, D., unpublished results.

(13) Gas-phase acidity data were taken from: Bartmess, J. E.; McIver, R. T., Jr. "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 11, pp 87–121.

(14) Olmstead, W. N.; Margolin, Z.; Bordwell, F. G. *J. Org. Chem.* **1980**, *45*, 3295–3299.

(15) Hofmann, J. E.; Muller, R. J.; Schriescheim, A. *J. Am. Chem. Soc.* **1963**, *85*, 3000–3002.

(16) Shapiro, I. O.; Ranneva, Yu. I.; Romanskii, I. A.; Shatenshtein, A. I. *J. Gen. Chem. USSR* (*Engl. Transl.* **1976**, *46*, 1132–1136.

(17) Arnett, E. M.; Johnson, D. E.; Small, L. E. *J. Am. Chem. Soc.* **1975**, *97*, 5598–5600.

(18) Stull, D. R.; Westrum, E. F., jr.; Sinke, G. C. "The Chemical Thermodynamics of Organic Compounds"; Wiley: New York, 1969. Calculations by Benson's group additivity method predict ΔH_0 to be −7.2 kcal/mol for this isomerization.[19]

(19) Benson, S. W. "Thermochemical Kinetics", 2nd ed. Wiley: New York, 1976; Table A.1.

(20) Bartmess, J. E., unpublished results privately communicated.

should be ca. 14 pK_a units less acidic than pyrrole, but it is actually 5.3 pK_a units *more* acidic. This provides a means of estimating the aromaticity of the cyclopentadienyl anion as 26 kcal/mol, which agrees reasonably well with estimates of 24 and 27 kcal/mol based on other models. The progressive increase in acidity along the series pyrrole, indole, carbazole is explained by increases in inductive and/or resonance effects resulting from the presence of an additional benzene ring(s). The reversal of this acidity order in the corresponding carbon acid series, cyclopentadiene, indene, fluorene, is explained by a progressive decrease in the aromatic stabilization energy of the cyclopentadienyl moiety, which overshadows the inductive and/or resonance effects of the additional benzene ring(s). Aromatic stabilization energies of 20 and 14.5 kcal/mol are estimated for the indenyl and fluorenyl anions, respectively.

Acknowledgment. We are grateful to the National Science Foundation for support of this research.

Registry No. 1,3-Cyclopentadiene, 542-92-7; indene, 95-13-6; fluorene, 86-73-7; pyrrole, 109-97-7; indole, 120-72-9; carbazole, 86-74-8; acetonitrile, 75-05-8; sulfonylbismethane, 67-71-0; (methylsulfonyl)benzene, 3112-85-4; methylbenzene, 108-88-3; methane, 74-82-8; cyanamide, 420-04-2; methanesulfonamide, 3144-09-0; benzenesulfonamide, 98-10-2; benzenamide, 62-53-3; ammonia, 7764-41-7.

Correlation of Gas-Phase Proton Affinities with S_N2 Nucleophilicities. A Quantitative Assessment of Steric Hindrance in S_N2 Reactions

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Received July 7, 1980

The factors underlying nucleophilicity of ions and molecules involved in S_N2 reactions have long held the interest of mechanistic chemists. By definition, nucleophilicity is the relative ability of an ion or molecule to donate a pair of electrons to assist displacement of a leaving group.[1] Yet correlation of this kinetic property with thermodynamic properties of the nucleophile, such as basicity and ionization potential, has generally been unsatisfactory. While poor correlation is probably a consequence of variations in solvation and steric factors,[1b,2-4] there has rarely been sufficient evidence to warrant firm assignment of a specific reason for poor correlation. Experimental sophistication and advances in experimental methods have produced new data which make a new attempt at such correlations timely.

Our interest in correlating nucleophilicity with some intrinsic property of the nucleophile was derived from our solvolysis studies of bulky secondary alkyl substrates in mixed solvents. There have been reports of inversion of the normal order of nucleophilicity in the aqueous ethanolysis of 1-octyl,[5] 2-octyl,[5] and 2-adamantyl[6,7] substrates.

Table I. Rate Constants, N Values ($MeOSO_2F$ Scale), and Proton Affinities for 3- and 4-Substituted Pyridines

substituent	relative proton affinity[a]	k_2, $MeOSO_2F$,[b] 25 °C, i-$PrNO_2$	nucleophilicity, N[c]
3-Me	2.7	8.84	0.22
H	(0.0)	5.36	(0.0)
3-Cl	−5.8	0.514	−1.01
3-F	−6.6	0.582	−0.96
4-CN	−10.5	0.204	−1.42

[a] Reference 18. [b] Reference 16. [c] Calculated using the Swain-Scott equation, $\log (k/k_0) = sN$ assuming $s = 1$, an arbitrary choice; cf. ref 8.

Table II. Rate Constants, N Values (EtI Scale), and Proton Affinities for 3- and 4-Substituted Pyridines

substituent	relative proton affinity[a]	$k_2 \times 10^4$, EtI,[b] 60 °C, $PhNO_2$	N[c]
4-MeO	6.7	8.20	0.42
4-Me	4.0	6.65	0.33
3-Me	2.7	6.35	0.30
H	(0.0)	3.15	(0.0)
4-Ac	−3.5	0.740	−0.63
3-Cl	−5.8	0.287	−1.04
4-CN	−10.5	0.107	−1.47
3-CN	−11.3	0.0531	−1.77

[a] Reference 18. [b] Reference 17. [c] Calculated using the Swain-Scott equation, $\log (k/k_0) = sN$, assuming $s = 1$.

In each instance, a new solvolysis mechanism was proposed to account for the inversed nucleophilic order. Peterson and co-workers[8] have argued that the 1-octyl and 2-octyl results are not unexpected based on the various factors which may influence nucleophilicity in such systems. Our own results for 2-octyl substrates[9] led us to suggest that steric factors were the primary cause of the inversion of nucleophilic order with the octyl derivatives.

Since steric factors are absent from gas-phase proton-exchange equilibria,[10] it was hoped that a plot of nucleophilicity vs. gas-phase basicity would unequivocally reveal steric factors operative on nucleophilic order. The major question was whether or not solvation effects would interfere in such a correlation.

Peterson[8] and Schleyer[11] and their co-workers have recently treated solvolytic reactivity of simple primary and secondary substrates in terms of major factors which affect solvolytic rate. Following the approaches advocated by Swain[12] and Winstein,[13] each group refined and evaluated equations designed to quantify, and thus separate, solvent ionizing power, substrate sensitivity, and nucleophilicity (N). None of the treatments quantified a nucleophile's sensitivity to steric factors. Despite this and the use of

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