sonic relaxation data for the trans to gauche conversion of 1,1,2-trichloroethane.[5] They are much larger than the 0.4% volume decrease estimated for methylcyclohexane (equatorial to axial) from density data.[6] Because lack of information about $\Delta\bar{V}$ for conformational changes has thrown doubt on the value of the acoustic method as a means for determining conformational energy changes,[5] results like those presented here should also be useful in interpreting ultrasonic absorption data.

The observed decreases in volume for conversion of the halogenated cyclohexanes from equatorial to axial forms probably reflect the relatively greater crowding of atoms in a as opposed to e conformers. Thus, the axial conformers have 1-3 (parallel) interactions between a bulky halogen atom and two hydrogen atoms, not present in the equatorial forms. It will be difficult to predict partial molar volumes of particular conformers from knowledge of their structures and van der Waals parameters, partly because of the complicating effects of packing solvent molecules around the individual solutes, but it may be possible to determine empirically the magnitudes of volume effects which are due to atomic contacts of particular types. Whether or not such effects are additive and transferable from compound to compound can only be determined when additional volume data of the type presented here become available.

Acknowledgment. Financial support from The Norwegian Research Council for Science and The Humanities is gratefully appreciated.

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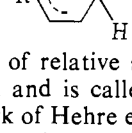
The Baker-Nathan Effect on Solvation Energies of Benzenonium and Other Organic Ions

Sir:

Hehre, McIver, Pople, and Schleyer[1] have recently presented conclusive evidence that in the gas phase alkyl groups follow the inductive order (Me < Et < *i*-Pr < *t*-Bu) in their ability to stabilize arenonium ions ($C_6H_6R^+$). A



$= (C_6H_6R^+)$

contrary ordering of relative stabilities has often been reported in solution and is called the Baker-Nathan effect. Thanks to the work of Hehre et al.[1] the origin of the inverted ordering can now be attributed unequivocally to solvation factors as was proposed originally by Schubert and Sweeney.[2] Combination of the gas phase data with heats of vaporization and heats of ionization of the alkyl benzenes in superacid solution allows calculation of the solvation enthalpies of the benzenonium ions.

Table I. Relative Enthalpies for Ionization and for Solution of Arenes and Arenonium Ions (in kcal mol^{-1})

Arene	$\delta\Delta H_i{}^a$ (gas)	$\delta\Delta H_i{}^b$ (ma)	$\delta\Delta H_S{}^c$ (C_6H_5R) (g → MeOH)	$\delta\Delta H_S$ ($C_6H_6R^+$)
C_6H_5Me	0.0	0.00	0.00	0.00
C_6H_5Et	−0.85 ± 0.1	2.84	−1.19	2.50 ± 0.75
C_6H_5-*n*-Pr	−1.7 ± 0.1	2.13	−1.87	1.96 ± 0.39
C_6H_5-*i*-Pr	−2.1 ± 0.1	2.61	−1.85	2.86 ± 0.58
C_6H_5-*t*-Bu	−2.3 ± 0.5	3.87	−2.57	3.60 ± 0.96

[a] From ref 1. Relative enthalpies of ionization in the gas phase (ΔH_i (gas)) are equated to observed standard free energies for $C_6H_5R + C_6H_6Me^+ \rightleftharpoons C_6H_6Me^+ + C_6H_5R$, in the opposite sense to the process reported in ref 1. [b] These values correspond to the relative heats for transfer from methanol at −60° to ma (11.5% SbF_5 in HSO_3F) at −60°. They differ slightly from those used in ref 1 which were based on earlier work from this laboratory using CCl_4 at 25° as a reference state. [c] The assumption that $\Delta G°_i$ (gas) = $\Delta H°_i$ (gas) is based on the reasonable assumption that $\Delta S°_i$ (g) = 0 for an isodesmic proton exchange reaction in the gas phase for a series of structurally similar compounds. It has some support from experiment (Kebarle) and carries the important implication that $\Delta H°_i$ (gas and $\Delta G°_i$ (gas) are temperature invariant since $(\partial G°/\partial T) = \Delta S°_i = 0$. [d] Values in this column were calculated through the type of cycle previously employed by us (E. M. Arnett, *Acc. Chem. Res.*, 6, 404 (1973)); thus $\delta\Delta H_S(C_6H_6R^+) = \delta\Delta H_i(\text{ma}) - \delta\Delta H_i(\text{gas}) + \delta\Delta H_S(C_6H_5R)$.

In Table I are presented the heats of ionization in the gas phase ($\delta\Delta H_i$(gas)), heats of ionization in 11.5% SbF_5-HSO_3F (magic acid) (ma) at −60° ($\delta\Delta H_i$ (ma)) the heats of solution at −60° ($\delta\Delta H_s$ (C_6H_5R) of the arene from the gas phase to methanol (the reference solvent), and finally the heats of solvation of the benzenonium ions ($\delta\Delta H_s$ $C_6H_6R^+$) from the gas phase into ma at −60°. All values are taken relative to toluene as reference compound and are derived from data in ref 1 or Table II.

In previous studies[3,4] heats of benzenonium ion formation were estimated using heats of transfer from CCl_4 at 25° to ma at −65°. The values presented here are based instead on methanol at −60° as the reference state. Although the choice of inert solvent should have a minor effect on the derived ionization or solvation energies, we believe that methanol is preferable since it is a liquid at −60° (CCl_4 freezes at −23°). Also methanol is probably a better medium as a model for the behavior to be expected of HSO_3F-SbF_5 if it could be divested of its protonating ability. Larsen, Bouis, and Glass[5] have shown that small Baker-Nathan orders for arenes can be generated merely through heats of transfer from solvents of low to high cohesive energy density (CED). We wish to minimize any such artifacts in the data presented here. In this sense, we believe that methanol should be a better model for HSO_3F than is CCl_4.

The heat of solution of a pure liquid solute in any solvent is actually the heat of transfer of the solute dissolved in itself to high dilution in the solvent in question. Since the CED's of the arenes decrease from 79.2 for toluene to 69.7 for *tert*-butyl benzene, it is reasonable to expect that heats of solution could change from a false "inductive order" in solvents of low CED to a false "Baker-Nathan order" in solvents of high CED since in the absence of internal energy changes

$$\Delta H_{\text{transfer}} \simeq [\text{CED}_{\text{solvent}} - (\text{CED})_{\text{ArR}}]_{\text{sol}} V_{\text{ArR}}$$

where V_{ArR} is the molar volume of the arene solute.

In contrast, transfer of a neutral, nonpolar solute from the gas phase to an inert solvent will result in an exothermic interaction which will increase in a regular progression as a

Table II. Experimental Data for Calculating Heats of Ionization in Magic Acid (ma) and Heats of Solution in Methanol at −60°. All values in kcal/mol

	$\Delta H_S{}^{-60°}$ (ma)	$\Delta H_S{}^{-60°}$ (MeOH)[f]	$\Delta H_S{}^{25°}$ (MeOH)[f]	$\Delta H_{vap}{}^{25°}$	$\Delta H_{-60}{}^{25°}$ (l)	$\Delta H_{-60}{}^{25°}$ H(v)	$\Delta H_i{}^{-60°}$	$\delta H_i{}^{-60°}$
C_6H_5Me	−5.0 ± 1.1[g]	−0.09 ± 0.04	0.35 ± 0.03	9.081[a]	2.983[h]	2.109[k]	−4.90	0.00
C_6H_5Et	−2.26 ± 0.58[g]	−0.20 ± 0.07	0.55 ± 0.02	10.10[b]	3.548[h]	2.608[k]	−2.06	2.84
C_6H_5-*n*-Pr	−2.70 ± 0.13[f]	+0.07 ± 0.06	0.35 ± 0.04	11.048[d]	(4.029)[j]	3.092[k]	−2.77	2.13
C_6H_5-*i*-Pr	−2.49[g] ± 0.3	−0.20 ± 0.08	0.37 ± 0.02	10.788[d]	(3.989)[j]	3.081[k]	−2.29	2.61
C_6H_5-*t*-Bu	−1.24[g] ± 0.3	−0.21 ± 0.08	0.70 ± 0.03	11.50[e]	4.541[i]	(3.634)[j]	−1.03	3.87

[a] J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds", Elsevier, Amsterdam, 1950. [b] The value given by ref *a* is 10.155 cal mol^{-1} at 20.85°; it has been corrected by using C_p (l) and C_p(v) from ref *a*. [c] Landolt-Börnstein, "Handbuch der Chemie", Springer-Verlag, Berlin, 1961. [d] N. S. Osborne and D. C. Ginnings, *J. Res. Nat. Bur. Stand.*, **39**, 468 (1947). [e] E. J. Prosen, W. H. Johnson, and F. D. Rossini, *ibid.*, **36**, 455 (1946). [f] This work. [g] E. M. Arnett and J. W. Larsen, *J. Am. Chem. Soc.*, **91**, 1438 (1969). [h] Using the values of C_p (T) given by ref *a*. [i] Using the values of C_p (T) given by H. M. Huffman, G. S. Parks, and A. C. Daniels, *J. Am. Chem. Soc.*, 52, 1547 (1930). [j] Estimated assuming that the difference between C_p (l) and C_p (v) is constant for these closely related compounds. [k] Using the values of C_p (v) at 25° given by ref *c*.

Table III. Solvation Enthalpies of Alkyl Substituted Organic Ions from the Gas Phase to Various Solvents

R	$C_6H_6R^+$ in magic acid[a]	$RNH_3{}^+$ in HSO_3F at 25°[b]	$RNH_3{}^+$ in H_2O at 25°[c]	RO^- in DMSO at 25°[d]	*p*-$RC_6H_5O^-$[f]	Molar volume in ml/mol
Me	0.00	0.0	0.0	0.0	0	106.3
Et	2.50 ± 0.75	1.30	0.1	6.2		122.5
i-Pr	2.86 ± 0.58	3.00	1.9	9.1		139.5
t-Bu	3.60 ± 0.96	3.90[e]	2.8	11.0	1.5[h] 4.9 ± 1.1[g]	155.9
CED of solvent in (cal/ml)	?	~150 (?)	530 (estd)	170		
Dielectric constant	?	~>100	79	50		

[a] This study. [b] E. M. Arnett and J. Wolf, *J. Am. Chem. Soc.*, in press. [c] E. M. Arnett, F. M. Jones, III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Am. Chem. Soc.*, **94**, 4724, (1972). [d] E. M. Arnett, L. E. Small, R. T. McIver, Jr., and J. S. Miller, *J. Am. Chem. Soc.*, **96**, 5638 (1974). [e] We have made a comparable measurement in magic acid at −60° which agrees within experimental error. [f] Unpublished results of Dr. L. E. Small. [g] Estimated values for *p-tert*-butylphenol from R. Dreisback, *Chem. Soc., Spec. Publ.*, No. 15 (1968). [h] Estimated value for *p-tert*-butylphenol (g) and measured value reported by J. B. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970, p 211.

Table IV. Differences between Enthalpies of Solvation between Ions Listed in Table III and Their Corresponding Neutral Bases

	$C_6H_6R^+$ (ma) − C_6H_5R (MeOH) at −60°	$RNH_3{}^+$ − RNH_2 (H_2O)	RO^- − ROH (DMSO)
Me	0.00	0.0	0.0
Et	3.69	2.0	6.77
i-Pr	4.71	4.60	9.81
t-Bu	6.17	5.8	10.9

function of molar volume,[6] dominated by an increase of 1-2 kcal/mol per CH_2 group. The heats of solution of the arenes from the gas phase to methanol (third column of Table I) display such an exothermic trend from toluene to *tert*-butylbenzene as would be expected for dispersion force interactions.[6] Therefore, the endothermic trend for the solvation enthalpies of the corresponding arenonium ions (ΔH_s ($C_6H_6R^+$)) must be the result of some volume factor which progressively reduces the solvation energy as the alkyl group becomes larger. Table III shows a remarkably parallel behavior between the effects produced by the "big four" groups on several types of ions both positive and negative. The ions are of different size and degrees of delocalization and are in different solvents.

The substituent effects observed here in each solvent are in the direction consistent with classical electrostatics—smaller ions give more exothermic solvation energies. However, we see no pattern in the variation of the solvation energies in Table III in response to changes in dielectric constant or to charge delocalization which would suggest a *simple* electrostatic interpretation even if it were theoretically appropriate.[7] In Table IV are listed the differences $\Delta H_s{}^g$ (ion) − $\Delta H_s{}^g$ (molecule) for the series shown in Table III. This provides a crude estimate of the true magnitude of the solvation factor in the ion which produces Baker-Nathan ordering using the neutral precursor as a model for the behavior of the ion. We favor the notion[2] that the reduction in solvation energy by increasing the bulk of the substituent has a steric origin. The dramatic difference between the effect of *tert*-butyl vs. methyl in the tightly localized alkoxy series and the delocalized phenoxy series is compatible with both points of view.

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(7) In a previous publication E. M. Arnett, L. E. Small, R. T. McIver, Jr., and J. S. Miller, *J. Am. Chem. Soc.*, **96**, 5638 (1974), noted that the results in column four of Table III were consistent with the Born equation in the sense that $\delta\Delta H_S{}^{g\text{-DMSO}}$ (RO^-) correlates with the reciprocal radius of the ion. Actually, the Born equation is not appropriate for the solvation of nonspherical, nonconducting ions in noncontinuous solvents. The poor performance of the Born equation in treating small spherical conducting ions is well documented (see A. K. Covington and T. Dickinson, Ed., "Physical Chemistry of Organic Solvent Systems", Plenum Press, New

York, N.Y., 1973, for several cogent discussions). The mere fact that the thermodynamic properties of solvation for an homologous series of organic ions are correlated with their reciprocal volumes or reciprocal radii cannot by itself justify the invocation of a simple electrostatic interpretation.

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Novel Activation Parameters and Catalytic Constants in the Aminolysis and Methanolysis of *p*-Nitrophenyl Trifluoroacetate[1]

Sir:

We wish to report here that the third-order reaction of *n*-butylamine with *p*-nitrophenyl trifluoroacetate is accompanied by substantial *negative* activation energies when carried out in both chlorobenzene and 1,2-dichloroethane solvents. Although small negative activation energies are known, we are not aware of any previous report of one of the present magnitude[2,3] (ca. −10 kcal). Table I records the third-order rate constants and activation parameters. Conventional stopped-flow kinetic methods have been used to obtain the kinetic results.

In contrast, a normal (but small) positive activation energy is observed for the methanolysis of *p*-nitrophenyl trifluoroacetate in aprotic solvent containing methanol. Rate constants obtained from 13.5 to 37.8° in 1,2-dichloroethane containing 4.92 *M* methanol give: E_a = 5.0 kcal; $\Delta G^\ddagger$ = 18.3 (298 °K); $\Delta H^\ddagger$ = 4.4 kcal; $\Delta S^\ddagger$ = −46.7 eu.

The aminolysis of *p*-nitrophenyl acetate in polar aprotic solvents has been studied recently by the groups of Watson and of Menger. Watson[4] reports the reaction to be catalyzed by general bases, but, rather than Brönsted law catalysis, the third-order catalytic constants are closely correlated by the hydrogen-bonding parameters, pK_{HB}.[5] Menger[6] has observed very large meta- and para substituent effects in the aminolysis of phenyl acetate esters in aprotic solvents. This and other observations have led Menger to conclude that the reaction proceeds through a zwitterionic tetrahedral intermediate.[6,7]

We have also found general base catalysis of the *n*-butyl aminolysis of *p*-nitrophenyl trifluoroacetate in aprotic solvents. First-order kinetics with respect to each ester, *n*-butylamine, and catalyst are observed. The third-order catalytic constants, however, do not follow the Brönsted catalysis law, as may be seen from the data of Table II. The only satisfactory correlation of the third-order catalytic constants which we have been able to find is shown in Figure 1, which illustrates application of eq 1 to the *n*-butyl aminolysis of *p*-nitrophenyl trifluoroacetate in 1,2-dichloroethane at 24.9°.

Table I. Rate Constants and Activation Parameters[a] for the Third-Order[b] *n*-Butyl Aminolysis of *p*-Nitrophenyl Trifluoroacetate

1,2-Dichlorethane[c]		Chlorobenzene[c]	
Temp, °C	$10^5 k_3$, M^{-2} sec^{-1}	Temp, °C	$10^5 k_3$, M^{-2} sec^{-1}
4.3	22.1	5.6	8.92
16.5	10.3	16.7	5.16
24.9	5.83	24.9	3.01
31.2	4.20		
E_a, kcal	−10.9	E_a, kcal	−9.9
$\Delta H^\ddagger$, kcal	−11.5	$\Delta H^\ddagger$, kcal	−10.5
$\Delta G^\ddagger$, kcal	9.62	$\Delta G^\ddagger$, kcal	10.02
$\Delta S^\ddagger$, eu	−70.9	$\Delta S^\ddagger$, eu	−68.9

[a] The standard temperature is 25°. [b] First order in ester and second order in amine. [c] Solvent.

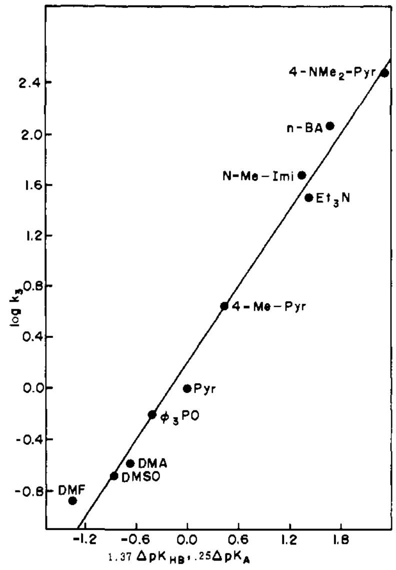

Figure 1. Correlation of the catalytic constants for the *n*-butyl aminolysis of *p*-nitrophenyl trifluoracetate by eq 1: ordinate, log k_3, in $Cl(CH_2)_2Cl$, 24.9°; abscissa, 1.37 ΔpK_{HB} + 0.25 ΔpK_A.

Table II. Catalytic Constants for the *n*-Butyl Aminolysis of *p*-Nitrophenyl Trifluoroacetate in 1,2-Dichloroethane, 24.9°

Catalyst	Log (k/k_0)	ΔpK_A	ΔpK_{HB}	Log $(k/k_0)_{calcd}$[a]
DMF[c]	−0.98	−6.51	0.18	−1.17
DMSO[d]	−0.68	−7.01	0.65	−0.66
DMA[e]	−0.59	−5.41	0.50	−0.46
$(C_6H_5)_3PO$	−0.20	−8.6	1.28	−0.19
C_5H_5N	(0.00)[b]	(0.00)[b]	(0.00)[b]	0.20
4-MeC_5H_4N	0.64	0.72	0.15	0.59
Et_3N	1.51	5.54	0.05	1.65
N-MeIA[f]	1.69	1.99	0.62	1.55
n-BuNH_2	2.07	5.43	0.23	1.87
4-N$Me_2C_5H_4N$	2.48	4.34	0.93	2.56

[a] Calculated from eq 1 with *a* = 1.37, *b* = 0.25, *c* = 0.20; SD = 0.14, SD/RMS = 0.101. If *a* is constrained to zero: *b* = 0.21, *c* = 0.79, SD = 0.51, SD/RMS = 0.386. If *b* is constrained to zero: *a* = 0.064, *c* = 0.56, SD = 1.19, SD/RMS = 0.900. [b] $k_0 = 4.96 \times 10^3$ $l.^2$ mol^{-2} sec^{-1}; pK_A = 5.21, H_2O, 25°; pK_{HB} = 1.88, CCl_4, 25°. [c] *N,N*-Dimethylformamide. [d] Dimethyl sulfoxide. [e] *N,N*-Dimethylacetamide. [f] *N*-Methylimidazole.

$$\log (k/k_0) = a\Delta pK_{HB} + b\Delta pK_A + c \qquad (1)$$

Pyridine has been taken arbitrarily as the reference catalyst with catalytic constant, k_0. ΔpK_A is the aqueous pK_A of the catalyst relative to that of pyridine. ΔpK_{HB} is the value of the hydrogen-bonding complex formation parameter of the catalyst relative to that for pyridine. The pK_{HB} scale has been generated[5] from the formation constants for hydrogen-bonded complex formation between *p*-fluorophenol and bases in CCl_4, 25°.

Table III summarizes the fitting parameters for eq 1 obtained from results such as those of Table II in the solvents chlorobenzene and 1,2-dichloroethane for both the *n*-butyl aminolysis and the methanolysis (a fixed methanol concentration of 0.495 *M* was used) of *p*-nitrophenyl trifluoroacetate.

The large *a*/*b* ratios for *n*-butyl aminolysis of *p*-nitrophenyl trifluoroacetate indicate that the energetics of hydrogen-bonded complex formation are dominant in the transition states for this reaction. The importance of proton