Lucken[40] and others,[41,42] an equation can be derived, $eQq/eQq_0 = -3\cos\alpha/(1-\cos\alpha)\{a-b\}$, where a and b are the populations of the nitrogen lone electron pair and the N–C bond population, respectively, and α is the C–N–C angle. Using the experimentally determined angle of 111°, and $eQq_0 = -9.0$ MHz[40] the value of $a-b$ can be calculated for free TMA and the complex. For free TMA it is 0.768. For the complex, using $eQq_{zz} = -3.760$, it is 0.528. These calculations show that the population difference is reduced by about 0.24 electron. Since the C–N bond is not likely to be the major source of the change in the electron density, this implies that the lone-pair electrons of the nitrogen partially transfer to the sulfur atom in the SO_2.

These estimates of charge transfer to sulfur are somewhat higher than from MO calculations[12,13] which give an increase of 0.15 electron at sulfur from the reported Mulliken population analysis. Of course, the dipole and quadrupole analyses neglected any corrections for vibrational averaging effects on the parameters, but the magnitude of these effects are not large enough to warrant detailed consideration given the simplicity of the models used to interpret them.

Centrifugal Distortion Constants. Interpretation of the distortion constants for asymmetric rotors is considerably more complex than for linear or symmetric top molecules. However, for weakly bonded complexes (≤5 kcal/mol), the largest contribution usually arises from the new stretching mode between the two moieties. Commonly the pseudodiatomic approximation which neglects contributions to the distortion constant D_J from all vibrational modes except the stretching mode is used to interpret the distortion constants.[43] Using this approximation and D_J in Table III, the stretching force constant was estimated to be 0.301 mdyn/Å, and the associated vibrational frequency was 129 cm^{-1}. Based on the Lennard-Jones 6-12 (LJ 6-12) potential, the binding energy was calculated to be about 4.5 kcal/mol which is much lower than the experimental value of 9.1 kcal/mol. This difference is partly due to the potential function which is used. It has been observed by Kollman et al. that the intermolecular interaction in many complexes is better approximated by setting the attractive term proportional to the inverse fifth power.[15] If we use this 5–10 potential form, the calculated binding energy of 7.1 kcal/mol agrees somewhat better. It is interesting that if we fit the calculated potential function for the complex in Figure 4 to a Lennard-Jones $n-2n$ form, a value of n of 3.15 (5) is estimated. This also shows that the repulsive wall is very soft and that the LJ 6-12 potential form is inappropriate as a binding model or to estimate the dissociation energy for this strong complex. Of course, the nearly $1/R^3$ dependence of the attractive term is close to a pure dipole–dipole term, also emphasizing the electrostatic interaction found in this complex. This reinforces the conclusion from the ab initio calculation and Morokuma decomposition procedure[15] which pointed out the importance of the electrostatic component in the overall binding energy for TMA-SO_2.

Acknowledgment. The authors acknowledge the help of Professors L. Lohr with ab initio calculations, C. E. Nordman with advice on crystal growing, and R. C. Taylor who supplied programs and advice on the vibrational analyses. They are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. The research was also supported by the National Science Foundation, Washington, DC.

Supplementary Material Available: Tables of hyperfine fitting of observed transition frequencies and centrifugal distortion fitting of the unsplit frequencies, Stark effect data, structure fitting data, thermal parameters, hydrogen atomic parameters, and ab initio binding energies and dipole moments (8 pages); listing of structure factors (4 pages). Ordering information is given on any current masthead page.

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Use of Gas-Phase Basicities for the Study of Solution Kinetics: An Unprecedented Extension of Brønsted Correlations

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Abstract: Activation free energies for the quaternization of N(sp^2 and sp^3) n-donor bases (B) with MeI in MeCN at 298 K (reaction i), $\Delta G^{\ddagger}_{MeI}$(MeCN), are linearly related to the standard free energy changes for the gas-phase protonation of the same bases (reaction ii), ΔG_{H^+}(g). These LFERs are compared to those relating ΔG_{H^+}(g) and the standard free energy changes

$$B + CH_3I \xrightarrow{MeCN} BCH^+_3 + I^- \quad \text{(i)}$$

$$B(g) + H^+(g) \rightarrow BH^+(g) \quad \text{(ii)}$$

for model donor–acceptor reactions in solution. These results shed light on important aspects of the Menshutkin reaction and strongly suggest that, *for processes not involving extensive charge dispersal from the solute to the solvent or strongly specific solvent–solute interactions, gas-phase basicities are the choice reference property for Brønsted analyses.*

Introduction

It has long been recognized[1] that alkylation of N(sp^2) and N(sp^3) n-donor bases (B) by alkyl halides (RX) in solution, a typical Menshutkin reaction[2] (eq 1), is a Lewis acid–base process.

$$B + RX \rightarrow BR^+ + X^- \quad (1)$$

Generalized Brønsted correlations,[3] i.e., linear relationships between the standard free energy change for the protonation of B

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in aqueous solution (reaction 2) and the standard activation free

$$B(aq) + H^+(aq) \rightarrow BH^+(aq) \quad (2)$$

energy change for reaction 1, are known to exist in the cases of the quaternization of 3- and 4-substituted pyridines,[4a-c] azoles,[4d] 4-substituted quinuclidines,[5a-c] and some primary amines.[5d] For these systems, both the basic center and the number of acidic hydrogens of the protonated species remain constant within each series.

In general, however, intrinsic structural effects on the aqueous solution basicity of nitrogen bases are dominated by large differential solvation effects of the protonated bases.[6] It is not surprising, therefore, that no generalized Brønsted correlations *of broad scope* (i.e., involving a wide variety of both sp^2 and sp^3 nitrogen bases) have heretofore been found in the case of Menshutkin reactions (MRs).[7]

We have just reported[8] the existence of extremely general, high-quality linear relationships between the standard free energy changes $\Delta G_{H^+}(g)$ and $\Delta G^\circ_{I_2}(soln)$ pertaining respectively to gas-phase protonation and to 1:1 charge-transfer[9] complexation of B with molecular iodine in "inert" solvents (eqs 3 and 4). With

$$B(g) + H^+(g) \rightarrow BH^+(g) \quad \Delta G_{H^+}(g) \quad (3)$$

$$B(soln) + I_2(soln) \rightarrow B\cdots I_2(soln) \quad \Delta G^\circ_{I_2}(soln) \quad (4)$$

this result in mind, the following reasons have led us to suspect that extended Brønsted correlations for MRs may also be generated by using $\Delta G_{H^+}(g)$ instead of $\Delta G^\circ_{H^+}(aq)$:

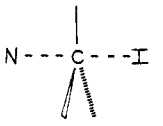
(1) Okamoto[10] has reported values of the second-order rate constants for the alkylation of ammonia and the methylamines with MeI in aqueous solution. The fact that the sequence of nucleophilicities is the same in water and in benzene and different from the ranking of aqueous basicities led Abraham[11] to conclude that the transition state of these reactions is more resemblant to the reactants than to the products. In particular, *this suggests the absence of strong interactions between the N–H bonds of the activated complex and the solvent.*

(2) As indicated by Salem,[12] Shaik,[13] and Pross and Shaik,[14] the transition state of the MR results from a HOMO–LUMO interaction involving the electron(s) of the nitrogen lone pair and the antibonding σ^* orbital of the alkylating agent (e.g., MeI). Our own ab initio studies on the MR fully support the donor–acceptor complex character of its transition state.[15]

This work is thus aimed at comparing gas-phase basicities [i.e., the negative of $\Delta G_{H^+}(g)$] of $N(sp^2)$ and $N(sp^3)$ n-donor bases with the activation free energies for their quaternization with MeI in MeCN at 298 K, $\Delta G^\ddagger_{MeI}(MeCN)$, reaction 5. Although iodine

$$B + CH_3I \rightarrow BCH_3^+ + I^- \quad (5)$$

is a bulky atom, in the activated complex of a MR what is "seen" by the N atom is a flattened,[16] relatively small methyl group (I),



I

Table I. Thermodynamic and Kinetic Data for Reactions 3 and 5[a]

base	δPA^{b-d}	$-\Delta G^\ddagger_{MeI}(MeCN)^{b,e}$
NH_3	0.0	0.0[h]
$MeNH_2$	9.6	2.09[i]
Me_2NH	16.7	3.31[i]
4-$((CH_3)_2N)C_5H_4N$	21.2	3.57[i]
DABCO[g]	23.6[f]	3.88[j]
4-cyanoquinuclidine	18.5	2.95[k]
quinuclidine	29.0	4.69[j]
c-$C_6H_{11}(N(CH_3)_2)$	28.5	2.63[l]
pyrazine	4.5	−2.68[m]
pyrimidine	6.8	−2.51[m]
pyridazine	11.5	−1.51[m]
pyridine(C_5H_5N)	16.8	−0.68[n]
4-$(CN)C_5H_4N$	5.7	−2.54[j,n]
4-$((CH_3)_2N)C_5H_4N$	32.4	1.24[j]
4-$((CH_3)_3C)C_5H_4N$	21.9	−0.24[j]
3-ClC_5H_4N	10.7	−2.24[n,o]
$C_6H_5(N(CH_3)_2)$	19.0	−1.14[p]
3-$(O_2N)C_6H_4(CH_3)_2$	10.1	−3.48[p]
3-$ClC_6H_4(N(CH_3)_2)$	18.0	−2.19[p]
3-$(CH_3)C_6H_4(N(CH_3)_2)$	20.6	−0.91[p]
4-$(CH_3)C_6H_4(N(CH_3)_2)$	21.1	−0.51[p]
4-$(CH_3O)C_6H_4(N(CH_3)_2)$	22.3	0.07[q]
1-methylimidazole	23.0	−0.25[r]

[a] All values in kcal·mol^{-1}. [b] Values corrected for symmetry changes as indicated in the text. [c] See ref 17b. [d] See ref 18. [e] At 298 K. [f] Reference 19. [g] 1,4-Diazabicyclo[2.2.2]octane. [h] Reference 20. [i] Reference 22. [j] Reference 23. [k] Reference 24. [l] Reference 25. [m] Reference 26. [n] Reference 28. [o] Reference 29. [p] Reference 30. [q] Reference 31. [r] Reference 32.

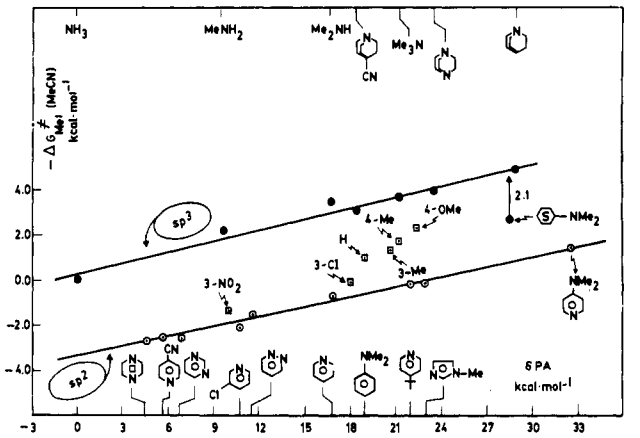


Figure 1. Plot of $-\Delta G^\ddagger_{MeI}(MeCN)$ vs δPA for the bases listed in Table I. Squares: *N,N*-dimethylanilines. All values are corrected for changes in symmetry numbers. δPA and $\Delta G^\ddagger_{MeI}(MeCN)$ are anchored to NH_3.

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so that front-strain effects are likely to be small in the majority of the cases studied herein. MeCN solutions have been chosen because of the availability of highly reliable recent data obtained in this solvent.

Results and Discussion

Table I summarizes the experimental values of $\Delta G_{H^+}(g)$ and $\Delta G^{\ddagger}_{MeI}(MeCN)$ anchored to ammonia [i.e., $\Delta G_{H^+}(g) = 0$ and $\Delta G^{\ddagger}_{MeI}(MeCN) = 0$ for NH_3]. Because symmetry numbers σ for B, BH^+, and the activated complex are often different,[17a] the magnitudes given in Table I and used heretofore are corrected for changes in σ. We note that the symmetry correction of $\Delta G_{H^+}(g)$ anchored to ammonia leads to relative proton affinities[17b] (δPA) defined as the standard enthalphy changes for reaction 6.

$$NH_3(g) + BH^+(g) \rightarrow NH_4^+(g) + B(g) \quad (6)$$

Figure 1 is a plot of $\Delta G^{\ddagger}_{MeI}(MeCN)$ vs δPA. It shows that $N(sp^2)$ and $N(sp^3)$ bases define two separate, nearly parallel linear relationships. The correlation equations defining these lines are as follows:

for $N(sp^3)$ bases

$$-\Delta G^{\ddagger}_{MeI}(MeCN) = (0.28 \pm 0.24) + (0.156 \pm 0.012)\delta PA \quad (7)$$

in kcal·mol^{-1}; $r^2 = 0.967$; $n = 7$; sd = 0.29 kcal·mol^{-1}

for $N(sp^2)$ bases

$$-\Delta G^{\ddagger}_{MeI}(MeCN) = -(3.19 \pm 0.14) + (0.143 + 0.009)\delta PA \quad (8)$$

in kcal·mol^{-1}; $r^2 = 0.970$; $n = 9$; sd = 0.22 kcal·mol^{-1}

These relationships are in fact more than "extended" Brønsted correlations: They should be considered as "true" correlations between $\Delta G^{\ddagger}_{MeI}(MeCN)$ and $\Delta G^{\circ}_{Me^+}(g)$, the latter being a model for solution values in which specific solvent–solute interactions are excluded. This is so because, for bases endowed with appreciable proton basicities (say comparable to or higher than that of NH_3), $\Delta G_{H^+}(g)$ and $\Delta G^{\circ}_{Me^+}(g)$ values are linearly related with essentially unity slope.[33] For pyridines, $\Delta G^{\circ}_{Me^+}(MeCN)$[28] and $\Delta G^{\ddagger}_{MeI}(MeCN)$ are related through eq 9. Similar correlations have been reported for other methyl cation exchanges[34] in solution.

$$\Delta G^{\ddagger}_{MeI}(MeCN) = (25.3 \pm 1.3) + (0.263 \pm 0.013)\Delta G^{\circ}_{Me^+}(MeCN) \quad (9)$$

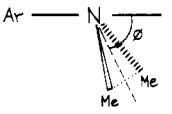
in kcal·mol^{-1}; $n = 6$; $r^2 = 0.963$; sd = 0.16 kcal·mol^{-1}

The correlations embodied in eqs 7 and 8 will predictably break down (i) when the slope of the relationship between $\Delta G^{\circ}_{Me^+}(g)$ and $\Delta G_{H^+}(g)$ is significantly different from unity and/or (ii) when the bases have large aromatic frameworks, as a result of a faster attenuation of polarizability effects in solution.[35]

Points for $EtNH_2$, i-$PrNH_2$, and t-$BuNH_2$ are off the line defined by eq 7, and the deviations increase with the extent of α-methyl substitution. In future work, we shall use this fact for a quantitative analysis of "steric" effects in MRs. At this point, we observe that the datum for *N,N*-dimethylcyclohexylamine is off the "sp^3 line" by 2.1 kcal·mol^{-1}, and we take this value as a reasonable estimate of the "steric" hindrance affecting 3- and 4-substituted *N,N*-dimethylanilines. Data for these compounds, corrected as indicated, are shown in Figure 1. We see that as the electron-donating ability of the substituents increases, there is a smooth evolution from a nearly "pure sp^2" to a "mixed sp^2–sp^3" behavior. This is obviously related to increasing pyramidalization of the basic nitrogen.[36]

These results raise questions, calling for more theoretical and experimental investigations:

(1) The rate of variation of $\Delta G^{\ddagger}_{MeI}(MeCN)$ with $\Delta G_{H^+}(g)$ for most *N,N*-dimethylanilines is much higher than that for "pure" sp^2 or sp^3 nitrogen bases (see Figure 1).[37] This suggests that the flip angle ϕ (see II) is a relevant contributor to the reaction



II

coordinate of the former. This effect has no counterpart in the case of bases having a "constant" hybridization.

(2) They stress the need for enthalphies of activation for the quaternization of most unhindered $N(sp^3)$ bases.[38]

Probably the most rewarding consequence of this "extended Brønsted" approach is that *it provides* (seemingly for the first time) *an overall appraisal of structural effects on the nucleophilicity of nitrogen bases involved in MRs. It thus appears as a powerful unifying principle.*

Acknowledgment. This work was supported by Grants PB87/0357 and PR84–0977 from the CICYT. Valuable discussions with Prof. M. H. Abraham (University College, London) are most appreciated. J.-L.M.A. dedicates his contribution to the memory of Mrs. María Teresa Abboud (née Mas Puig).

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(38) To our knowledge, activation enthalpies are only available for the alkylation of DABCO and quinuclidine.