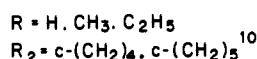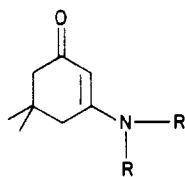## Unique Basicity Properties of Conjugated Amino Cyclohexenone Derivatives. The Effects of Molecular Structure on the Disparate Basicities toward H Acids[1]

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**Abstract:** Results are reported which show the uniquely high carbonyl basicities of conjugated amino cyclohexenones. An explanation is offered in terms of a general treatment of the effects of molecular structure on basicity.

We wish to report that the class of conjugated amino cyclohexenones represented by **I** have hydrogen bond acceptor (HBA) strengths and gas-phase proton-transfer basicities which are uniquely large. For example, when R = $CH_3$ the HBA strength on the $\beta$ scale[3] is 1.04, essentially equal to that for $[(CH_3)_2N]_3PO$ with the largest known $\beta$ value for any neutral base. Further, this same class **I** compound has a protonic gas-phase basicity[4] which is 7.1 kcal/mol (5.2 log units) greater than the previously known most basic oxygen compound, 4-(dimethylamino)acetophenone.[9]



**I**

R = H, $CH_3$, $C_2H_5$
$R_2$ = c-$(CH_2)_4$, c-$(CH_2)_5$[10]

In another paper (with M. J. Kamlet), a general treatment of the effects of molecular structure on basicity will be presented.[11,12] Here we communicate results and brief interpretations for class **I** compounds. This is of timely importance because the relatively low aqueous $pK_{a(BH^+)}$ values ($\sim 3.0$) but high $\beta$ values ($\sim 1.0$) for class **I** bases permit the formation of stable H-bonded and metal ion[14] complexes under even mildly acidic conditions (aqueous or biological media) where for "normal" strong bases such complex formation is excluded by the formation of the conjugate acid $BH^+$.

In the absence of significant steric effects or the formation of cyclic chelates between internal HBA and HBD groups, molecular basicity of most kinds can be treated as a function of four effects:[12] the atomic center which acts upon the lone pair electrons (parameterized by us[3,11] as $\xi$ values) and the field/inductive (F),

resonance (R), and polarizability (P) effects[7] of the more distant substituent groups. For neutral N and O bases, decreasing va-

(1) This work was supported in part by a grant (to R.W.T.) from the National Science Foundation.

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(3) Cf.: Kamlet, M. J.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877; *J. Soln. Chem.* **1985**, *14*, 153. The formation constants, $K_f$, for 1–1 H-bonded complexes for bases with a given reference acid very frequently (but not always) obey the following equation: $\log K_f = c + b\beta$, to a precision of ±0.04 or less $\beta$ units. Exceptions are discussed in ref 11.

(4) In this paper all gas and aqueous phase basicities (unless otherwise stated) are given in $\log K_b$ units at 298 K, for the proton transfer equilibrium $B + NH_4^+ \rightleftarrows BH^+ + NH_3$; $-\Delta G°_{298}/1.364 = \log K_b$. Gas-phase basicities have been obtained by previously reported methods[5-7] using at least four well-established standard bases for each, two of which were more basic and two less basic. The precision of all $\Delta G°$ values is ±0.2 kcal/mol or less. The detailed results will be given in a following paper, or prior to publication they may be obtained from R. W. Taft. Proton affinities may be obtained by converting $\Delta G°$ to $\Delta H°$ values using $\Delta S°$ values obtained as described in the above references, together with the currently accepted[8] $PA(NH_3) = 204.0$ kcal/mol ($PA(B) = 204.0 - \Delta H°(B)$). Aqueous $\log K_b$ values are based upon $pK_a$ or $\Delta G°$ values given in standard references as cited in ref 7.

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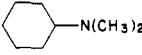(8) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.
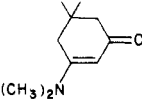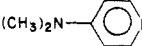
(9) Like for class **I** bases (cf. discussion), *gas-phase protonation* occurs preferentially at oxygen to form the conjugated ion. This is shown by the fact that $p$-N($CH_3$)$_2$-substituted acetophenone is one power of ten more basic than is its meta isomer. Para isomers of aromatic bases with $\pi$ electron acceptor substituents, e.g., $CO_2R$, CN, COR, and $NO_2$, are always *less* basic in the gas phase than their meta isomers (unless instead the substituent is the preferred protonation site); Mishima, M.; Taft, R. W., paper in preparation. However, unlike class **I** bases, $p$-N($CH_3$)$_2$-substituted acetophenone in aqueous solution protonates on nitrogen. This results from the particular interplay of effects discussed herein.

(10) The following $\log K_{b(g)}$ and $\beta$ values, respectively, have been obtained: R = H, 15.6, 0.95; R = $CH_3$, 21.6, 1.04; R =$C_2H_5$, 24.2, 1.06; $R_2$ = c-$(CH_2)_4$, 24.4, 1.06; $R_2$ = c-$(CH_2)_5$, 24.1, 1.06. For aqueous proton transfer basicities, cf. ref 13.

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862   *J. Am. Chem. Soc., Vol. 108, No. 5, 1986*

*Taft et al.*

**Table I.** Comparisons of the Gas- and the Aqueous-Phase Proton-Transfer Basicities and the Hydrogen Bond Acceptor Basicities Relative to Ammonia

| | base, B[a] | log $K_{b(gas)}$[b,e] | log $k_{b(aq)}$[b] | $\beta_{(B)} - \beta_{NH_3}$[c] |
|---|---|---|---|---|
| 1 | CH₃CH=O | -13.6 | est -14.5[d] | -0.11 |
| 2 | (CH₃)₂O | -8.5 | -11.7 | +0.01 |
| 3 | ⬡=O | -1.2 | ca -12.6 | +0.04 |
| 4 | NH₃ | 0.0 | (0.00) | (0.00) |
| 5 | C₆H₅COCH₃ | 1.2 | -13.6 | 0.00 |
| 6 | ⬡=O | 3.1 | -12.4 | 0.11 |
| 7 | CH₃CON(CH₃)₂ | 9.4 | -9.7 | 0.27 |
| 8 | ⬡N | 12.9 | -4.0 | 0.15 |
| 9 | ⬡—N(CH₃)₂ | 21.5 | 1.5 | 0.21 |
| 10 | (CH₃)₂N—⬡=O | 21.6 | -6.1 | 0.55 |
| 11 | ⬡N | 21.8 | 1.9 | 0.27 |
| 12 | (CH₃)₂N—⬡—N | 24.3 | 0.6 | 0.38 |

[a] ξ values from reference 11 are the following: >P=O, -0.20; >C=O, 0.0; >O, 0.20; N(sp²) 0.60; >N, 1.00. [b] log $K_b$ is defined in footnote 4. [c] β values are from ref 3 or this work. For NH₃, β = 0.49.[12] [d] Calculated from the following equation:[11] $pK_{a(BH^+)} = -10.2 + 12.8\beta + 11.5\xi$. [e] Values obtained in this work are for bases 6, 9, and 10; all others are from data given in ref 5-7.

lence-state electronegativity[15] acting on the lone pairs leads to large basicity increases,[16,17] i.e., O(sp²) < N(sp) < O(sp³) < N(sp²) < N(sp³). Substituent π electron donating resonance effects strongly increase basicity whereas effects from dipolar substituents or from substituents of decreasing polarizability quite frequently strongly reduce basicity by decreasing charge stabilization in the acid–base complex.[7] The relative magnitudes of the contributions of these four effects depend markedly, however, upon the reference acid and the reaction conditions.

Gas-phase proton-transfer basicities have particularly large dependences upon both the ξ and the substituent polarizability values.[12] HBA basicities have particularly small dependences on these same two effects.[11,12,17] Aqueous proton-transfer basicities have similar small dependences on substituent polarizability effects but have relatively large dependences upon ξ, R, and F effects and, in addition, involve very large aqueous medium hydration effects.[9] Table I illustrates these relationships, as well as preferred protonation site considerations, for the above three kinds of basicities toward H acids, by comparisons for eleven typical bases, each relative to NH₃.

First, consider the preferred gas-phase protonation sites in **7, 10,** and **12** of Table I. From family substituent effect studies,[8] one may estimate that for N protonation (to give the unconjugated ion) the basicities would be at least 18, 8 and 8 powers of ten less than for C₂H₅NMe₂, (c-C₆H₁₁)NMe₂ and (c-C₆H₅)NMe₂, re-

(11) For preliminary reports cf. ref 3 and the following: Kamlet, M. J.; Gal, J. F.; Maria, P. C.; Taft, R. W. *J. Chem. Soc., Perkin Trans 2* **1985**, 1583.

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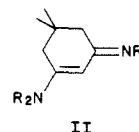
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**Table II.** Basicity Related Properties[a]

| property | I (R = C₂H₅) | CH₃CON(CH₃)₂ |
|---|---|---|
| PA,[b] kcal/mol | 236.0[b] | 215.8[b] |
| aq p$K_a$ (BH⁺) | 3.3[c] | -0.4 |
| β | 1.06[d] | 0.76[e] |
| $-\Delta H_{BF_3}(CH_2Cl_2)$, kcal/mol | 32.2[c] | 26.8[d] |
| log $P_{(o/w)}$ | 0.83[f] (1.0)[f] | -0.77[g] (+2.5)[g] |
| $-\Delta H_{(B)}$[g→aq], kcal/mol | 26.6[h] (±0.5) | 16.0 |
| $-\Delta H_{(BH^+)}$[g→aq], kcal/mol | 60.0[i] | 65.0 |
| $-\Delta H_{(ge)}$(BH⁺+H₂O), kcal/mol | (10.2)[k] | 16.5[j] (15.4)[k] |

[a] Unless otherwise cited, cf. ref 7. [b] Proton affinity, cf. 4. [c] Cf. ref 13. [d] Calculated from values of PA, log $K_{b(aq)}$, and heat of dissociation of BF₃ adduct in CH₂Cl₂ solution,[13] $-\Delta H_{BF_3}(CH_2Cl_2)$, using equation of the form $P = P_0 + b\beta + e\xi$, from ref 11, with a polarizability effect correction for PA. The values obtained agree to ±0.01. [e] Reference 3. [f] Logarithm of the partition constant between octanol and water for R₂ = c-(CH₂)₅, measured by C. Hansch and A. Leo, private communication. [g] From tables of Hansch and Leo (cf.: Kamlet, M. J., et al. *J. Am. Chem. Soc.* **1984**, *106*, 464). The value in parentheses is that calculated from the slightly modified equation of these authors given by Taft, R. W., et al. (*J. Pharm. Sci.* **1985**, *74*, 807), for the hypothetical substance having the π* and β values of DMA but the approximate molar volume, $\bar{V}$, of I with R₂ = c-(CH₂)₅. [h] Heat of transfer from gas phase to dilute aqueous solution obtained as the difference between the enthalpy of dissolution of solid base I (R = C₂H₅), -1.8 kcal/mol, and the enthalpy of sublimation (+24.8 ± 0.5 kcal/mol). The latter was obtained as the sum of $\Delta H_{vap}$ and $\Delta H_{fus}$. $\Delta H_{vap}$ was measured at 332.6 ± 0.2 K (as 20.4 ± 0.4 kcal/mol) with a CALVET microcalorimeter fitted with a Knudsen effusion cell (Sabbah, R.; Minadakis, C. *Thermochim. Acta.* **1981**, *43*, 269). $\Delta H_{fus}$ was measured with a Setaram DSC111 differential scanning calorimeter (4.4 ± 0.1 kcal/mol at 320.2 K). [i] Obtained from the thermodynamic cycle of ref 7 with use of the enthalpy of protonation of I (R = C₂H₅), -2.1 kcal/mol, which is the difference in the enthalpies of dissolution of the solid base in 0.1 M HCl (-3.9 ± 0.2) and in pure water (above). [j] Enthalpy of binding of BH⁺ to a water molecule in the gas phase; Mautner, M. *J. Am. Chem. Soc.* **1983**, *105*, 1257, 1265. [k] Calculated from the modified Mautner relation (ref j), $-\Delta H_{(g)}$(BH⁺+H₂O) = 72.3 - 0.26(PA), which holds to ±0.7 kcal/mol for 12 widely varying >C= OH⁺ ions. [l] Value calculated by eq 11 of Taft et al., ref g, using β = 1.06, $\bar{V}/100 \simeq 2.1$, and π* ≈ 1.3. The agreement between observed and calculated values may be taken as the fourth independent determination of β = 1.06 ± 0.03.

spectively, or log $K_{b(g)}$ values (Table I) would be for **7**, ~0, for **10**, ~14, and for **12**, ~7. The very much greater observed than estimated gas-phase basicities indicates that protonation must occur to give the conjugated cation in all three cases. The differences in log $K_{b(g)}$ values between **7** and **1** (23.0), between **10** and **6** (18.5), and between **12** and **8** (11.4) are indeed reasonable for basicity enhancing R and P effects of the NMe₂ substituent. The regular reduction in the above values corresponds to the increasing distance of separation between the conjugated NMe₂ substituent and the protonated atom. For **1, 7** and **6, 10,** it is clear that vinylogy principle is followed. Similar arguments (as well as spectroscopic evidence[13]) can be made for the same preferred sites of HBA and aqueous proton-transfer basicities for **7, 10,** and **12** (but not necessarily for other bases[9]).

Although the R effect (in particular) of the NR₂ substituents in class I bases leads to relatively large gas-phase proton-transfer basicities, the protonation on the highly electronegative O(sp²) atom opposes this R effect, preventing even greater log $K_{b(g)}$ values.[18] This is evidenced by the fact that both **11** and **12** have somewhat larger log $K_{b(g)}$ values than **10**. Protonation occurs at

(18) As expected from the smaller N than O electronegativity, the gas-phase proton-transfer basicity of [(CH₃)₂N]C=NH (log $K_b$ = 27.6) is 20 kcal/mol greater than that for [(CH₃)₂N]₂C=O (log $K_b$ = 13.0); unpublished result of F. Anvia and R. W. Taft. On this basis, class II compounds may be expected to be superbases having log $K_b$ values in the range 30-40:

⬡=NR'  R₂N

II

N(sp³) to form an unconjugated ion with **11** and at N(sp²) atom to form a less well conjugated ion with **12**. On the other hand, **10** has the largest $\beta$ value in Table I, i.e., this base (as well as other class I bases) has distinctly higher HBA basicity than most other known bases. This is accounted for by the relatively small dependence of HBA basicity on the valence-state electronegativities.

For inherently rather unstable bare ions, e.g., $CH_3C(=OH^+)H$ and $NH_4^+$,[19] bulk hydration energies are both large ($\sim 80$ kcal/mol)[7] so that $\log K_{b(aq)} \simeq \log K_{b(g)}$ for **1** and **4**. However, with increasing internal stabilization of $BH^+$ (as for all other bases of Table I), bulk hydration energies tend to become much smaller than for $NH_4^+$ so that $\log K_{b(aq)}$ becomes much less than $\log K_{b(g)}$. Indeed, for class I base **10**, the value of $\log K_{b(aq)}$ is less than $\log K_{b(g)}$ by a huge 28 units. Thus, an explanation has been provided for the basicity properties of class I compounds which were noted in the introductory statement. In support of this explanation, the following additional points may be made. There are no general correlations[20] between $\log K_{b(aq)}$ values and the corresponding values of either $\log K_{(g)}$ or $\Delta\beta$ of Table I. In spite of this, one finds *within a given family of bases* that if substituent polarizability effects are small or approximately constant there is the same sequence for all three kinds of basicity, e.g., $1 < 3 < 6 < 7 < 10$, $5 < 7, 8 < 12$, and $9 < 11$. Also, if R, F, and P substituent effects are all relatively small or constant, the $\xi$ order tends to emerge for all three basicity kinds, e.g., $6 < 8 < 9$ and $1 < 2$.

In Table II eight basicity related properties are compared for the typical amide, *N,N*-dimethylacetamide, with the class I base $R = C_2H_5$ (or the very similar $R_2 = c\text{-}(CH_2)_5$. In all cases the class I base is shown to be distinctly stronger (which may be attributed largely to the much greater basicity of the "parent" base of the latter (**6**) compared with that of the former (**1**),- cf. Table I). All of the relevant properties of Table II are in excellent accord with the value of $\beta = 1.06$ for the class I base.[21] For example, the exothermicity of transfer of this base from the gas to dilute aqueous phase (26.6 kcal/mol) is the largest value yet reported for a neutral base (cf. Table 24 of ref 7). As expected for the conjugate acid of such a strong HBA base, the corresponding exothermicity of transfer of this HBD ion (60 kcal/mol) is the smallest value yet reported for a $BH^+$. This pair of observations is nicely consistent with the earlier observation that values of the difference $\log K_{b(g)} - \log K_{b(aq)}$ are uniquely large for class I bases.

(19) The reader should appreciate that bare $NH_4^+$ is not the familiar form which is greatly stabilized by hydration or by ion aggregation. This may be appreciated by noting that log $K_b$ values in Table I indicate that bare $NH_{4(g)}^+$ quantitatively protonates acetophenone whereas $NH_{4(aq)}^+$ quantitatively does not. We are indebted to a referee for suggesting clarification on this point.

(20) For log $K_{b(g)}$, values increase in the sequence **1**–**12**; for log $K_{b(aq)}$ the sequence is $1 < 5 < 3, 6 < 2 < 7 < 10 < 8 < 4 < 12 < 9 < 11$; for $\beta$ values the sequence is $1 < 2, 4, 5 < 3 < 6 < 8 < 9 < 7, 11 < 12 < 10$.

(21) The gas-phase proton-transfer basicity of $[(CH_3)_2N]_3PO$ (whose $\beta = 1.05 \pm .01$ also) has been reported[22] as log $K_{b(g)} = 17.7$, which is 3.9 units less than that for **10**. This result is consistent with the lower $\xi$ value for P=O, than, C=O (ref 3).

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# Vibrational Spectra and Assignments of MeMn(CO)₅ and MeRe(CO)₅ Species, Energy-Factored and A₁ Force Fields, and a Further Effect of Free Internal Rotation

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**Abstract:** The infrared spectra of $^{12}CH_3$, $^{13}CH_3$, $^{12}CD_3$, and $^{13}CD_3$ species of MeMn(CO)₅ and MeRe(CO)₅ have been studied in the gas phase to 450 cm⁻¹ and in the solid at 78 K down to 200 cm⁻¹. Solid-phase Raman spectra (600–300 cm⁻¹) for MeRe(CO)₅ are also reported. Nearly all of the $\delta$(MCO) and $\nu$(MC) modes are assigned with confidence in both compounds, and two reassignments are proposed for MeMn(CO)₅. An energy-factored force field is calculated for the CO stretching vibrations by using gas-phase data which include the B₁ fundamental. An A₁ force field for all vibrations shows that all the metal–carbon bonds increase in strength from Mn to Re, while the methyl CH bond is weakened. The axial and equatorial M–CO bonds in MeRe(CO)₅ are equal in strength, suggesting a negligible trans effect on the part of the methyl ligand. This is interpreted in terms of equal and opposite $\pi$- and $\sigma$-trans effects, the former strengthening the axial Re–CO bond and the latter weakening it. The gas-phase contour of the absorption complex assigned to $\rho(CH_3)$ in MeRe(CO)₅ resembles those due to $\nu_{as}(CH_3)$ and $\nu_{as}(CD_3)$ and is attributed to a variation in the rocking force constant with internal rotation angle, together with free internal rotation. The corresponding band in MeMn(CO)₅ may also reflect the same effect.

In a previous paper[2] we discussed the infrared spectra of $^{12}CH_3$, $^{13}CH_3$, $^{12}CD_3$, $^{13}CD_3$, and $CHD_2$ labeled species of MeMn(CO)₅ and MeRe(CO)₅ in the CH and CD stretching frequency regions, with reference to the effects of free internal rotation on these bands

in the gas phase. In this work we report new infrared gas- and solid-phase data for MeMn(CO)₅ species, which complement the extended study recently published by Andrews et al.[3] and assign vibrations in the 700–300-cm⁻¹ region, leaning heavily on previous work and on similar studies of BrMn(CO)₅[4] and M(CO)₆ (M =

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