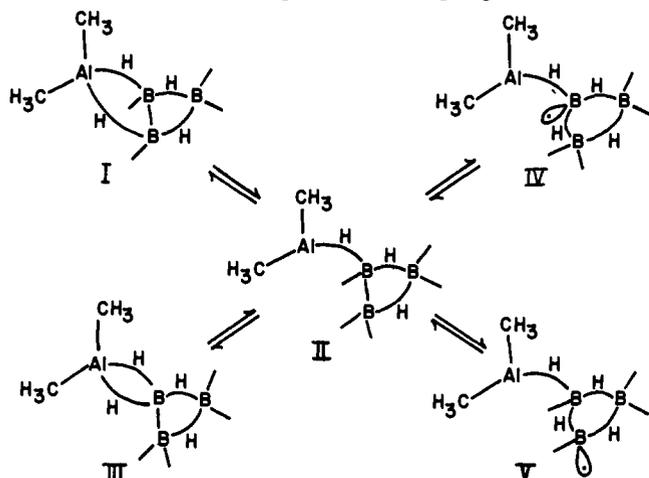around the B_3H_8 moiety while maintaining the CH_3 exchange. Further spectroscopic and chemical studies of these and related compounds are in progress.

JorJan Borlin, Donald F. Gaines*

*Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706*

Gas-Phase Basicities and Pyridine Substituent Effects[1]

Sir:

The substantially lower base strength toward the aqueous proton of pyridine ($pK_a = 5.21$) than that of ammonia and aliphatic amines ($pK_a = 9-11$) has generally been ascribed to a greater degree of s character in the former's hybrid molecular orbital containing the lone electron pair. We wish to report that in the gas phase the basicity is substantially greater for pyridine (proton affinity, $PA = 225 \pm 2$ kcal)[2] than ammonia ($PA = 207 \pm 3$ kcal)[3] and comparable with aliphatic amines,[4] *e.g.*, $(CH_3)_2NH$ ($PA = 225 \pm 2$ kcal). This observation clearly establishes that the stability afforded the pyridinium ion by differential polarization[5] of the π molecular orbital between gas and aqueous phases, as well as other solvation effects,[6] is as large or larger than the hybridization effect.

Such a substantial inversion in base strengths of ammonia and pyridine between gas and aqueous phases makes substituent effects on gas-phase proton affinity particularly significant. Do substituent constants, based upon observations in aqueous solution, apply in

(1) This work was supported in part by grants from the Public Health Service, the National Science Foundation, and the Atomic Energy Commission.
(2) W. L. Jolly, University of California, LBL-182, 1971, p 15, has estimated PA = 222 for C_5H_5N based upon core electron binding energies from X-ray photoelectron spectroscopy. The agreement is in apparent support of the concept of equivalence of equally charged cores.
(3) M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, 73, 4328 (1969).
(4) W. G. Henderson, J. L. Beauchamp, and R. W. Taft, unpublished results.
(5) The polarization of the π molecular orbital of pyridinium ion is an effect analogous to polarization of alkyl groups in ammonium ions. The latter effect has been shown to be of importance in the PA of aliphatic amines: *cf.* J. I. Brauman, J. M. Riveros, and L. K. Blair, *J. Amer. Chem. Soc.*, 93, 3914 (1971).
(6) (a) A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1293 (1949); (b) R. G. Pearson and D. C. Vogelson, *J. Amer. Chem. Soc.*, 80, 1038 (1958); (c) F. E. Condon, *ibid.*, 87, 4481 (1965).

the gas phase? What is the quantitative attenuation of substituent effects due to aqueous solvent? How useful are approximate molecular orbital treatments in such problems?

We have made a CNDO/2 calculation[7] of the relative proton affinities of 4-substituted pyridines using conventional geometries and bond distances. These calculations show a rough linear potential energy–free energy relationship between the calculated gas-phase proton affinities and the corresponding experimental free energies of aqueous ionization of slope ~ 3.6 (*cf.* Table I).

Table I. 4-Substituent Effects

	Aqueous solution		Gas phase	
Substituent	pK_a	$\delta_R \Delta G°$, kcal	$\delta_R \Delta E$,[c] kcal	$\delta_R PA$, kcal $\pm$ 2.0
MeO	6.58[a]	1.87	5.6[d]	8.0
Me	6.03[a]	1.12	6.9	5.0
H	5.21[a]	(0.00)	(0.0)	(0.0)
CF₃	2.63[b]	−3.52	−15.3	−11.0
NO₂	1.39[a,e]	−5.21	−21.4	−17.0

[a] A. Fischer, W. J. Galloway, and J. Vaughan, *J. Chem. Soc.*, 3591 (1964). [b] H. B. Yang, unpublished result. We are indebted to Dr. W. A. Sheppard for a sample. [c] CNDO/2 calculation. [d] Calculation for OH. [e] We are indebted to Dr. J. Lyle for a sample.

PA's have been determined using ion cyclotron resonance intensity–pressure plots[8a] and double resonance techniques[8b] with aliphatic and fluoroaliphatic amine standards which have been separately established.[4] Each pyridine was compared to at least three standards and its assigned PA is that of the amine for which proton transfer was observed with negative $(dk/dE_{ion})_0$ in both directions. Relative values of PA, $\delta_R PA$, for the 4-substituted pyridines are listed in Table I.

Figure 1 illustrates the satisfactory linear enthalpy–free energy relationship which exists between gaseous $\delta_R PA$ and aqueous $\delta_R \Delta G°$. The slope of this relationship, 3.5 ± 0.5, provides the first quantitative measurement on protonation equilibria of the attenuation in the effects of distant substituents due to the aqueous medium. The extent of agreement with the CNDO/2 calculation supports the predictive value of the method in this application. The attenuation factor may be attributed to three effects: (a) the higher effective dielectric constant[9] in the aqueous phase and the hydration of (b) the pyridines[6c] and (c) the pyridinium ions[6] by hydrogen bonding. The latter interactions lead to partial protonations of the pyridines and partial deprotonations of the pyridinium ions. Each of the three effects evidently involves a proportionality with the intrinsic (gas phase) base strengths, thus accounting for the linearity of Figure 1.

The substituent effects on ionization of 4-substituted pyridinium ions, H_2O, 25°, between various treatments, are best fitted by the relationship:[10] $\log (K/K_0) = 5.15\sigma_I + 2.69\sigma_R^+$. Converting the PA's to log K units gives for gaseous ionization: $\log (K/K_0) =$

(7) *Cf.* J. A. Pople and M. Gordon, *ibid.*, 89, 4253 (1967).
(8) (a) D. Holtz and J. L. Beauchamp, *ibid.*, 91, 5913 (1969); (b) J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, 48, 1783 (1968).
(9) J. G. Kirkwood and F. H. Westheimer, *ibid.*, 6, 506 (1938).
(10) S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, unpublished results.

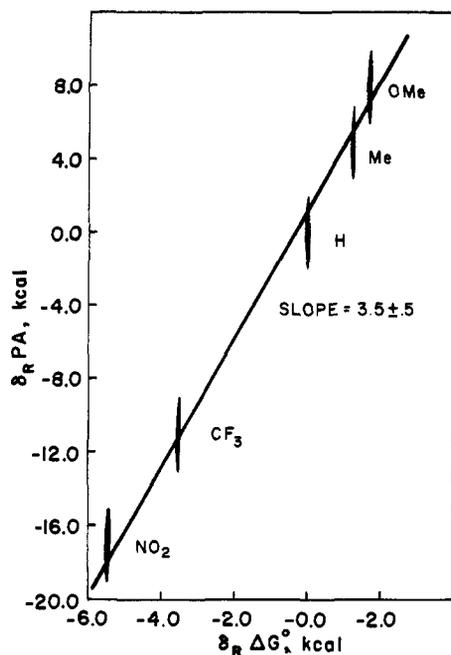Figure 1. Linear enthalpy–free energy relationship between gas and aqueous proton affinities of 4-substituted pyridines.

Figure 1. Molecular orbital diagrams for the σ orbitals of (a) SF_6, (b) PF_5, and (c) XeF_6 showing the occurrence of nonbonding orbitals and the mixing of the atomic s orbital with the ligand nonbonding orbitals. Filled-in circles indicate electrons in the final bonding scheme while open circles indicate electrons before s mixing. The ordering and splittings are schematic only. The two a_1' orbitals of PF_5 refer to the orbitals symmetric in the equatorial plane and along the threefold axis, respectively.[5]

$16.7\sigma_I + 10.3\sigma_R^+$. These results suggest the attenuation in ρ_R (3.83) may be greater than in ρ_I (3.25), but at present both factors are not reliably different from the 3.5 mean.

Our results clearly establish that in spite of reversals in basicity between gas and aqueous phases, as seen for NH_3 and pyridine, a linear enthalpy–free energy relationship does exist for 4-substituted pyridines. It may be anticipated that similar correlations involving other appropriate proton-transfer equilibria will be found in which there are markedly larger substituent effects in the gas than aqueous phase.

M. Taagepera, W. G. Henderson, R. T. C. Brownlee
J. L. Beauchamp, D. Holtz, R. W. Taft*

*Department of Chemistry, University of California
Irvine, California 92664*

Noyes Laboratory of Chemical Physics[11]
*California Institute of Technology
Pasadena, California 91109*

Received November 15, 1971

The Role of Nonbonding Orbitals, s Mixing, and d-Orbital Participation in Hypervalent Molecules

Sir:

Recently we presented[1] a simple valence-shell-electron bonding theory of hypervalent molecules, *i.e.*, those molecules formed from main-group elements in their higher valences. As this was part of an experimentally oriented article, we did not present the theory in molecular orbital language but rather provided the more transparent bond–orbital description. Most recently, a number of SCF-type calculations on individual molecules such as SF_6, PH_5, and ClO_4^-

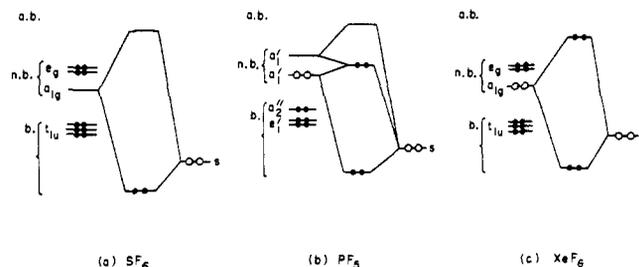(1) J. I. Musher, *Angew. Chem., Int. Ed. Engl.*, **8**, 54 (1969).

have been performed[2-7] and this prompts a sketch of the molecular orbital version of the general theory which provides a useful framework for considering the detailed calculations and their implications.

Multicenter bonding of molecules occurs whenever more bonds are formed to a given atom than atomic orbitals are available to form these bonds, *i.e.*, whenever a valence is greater than that given by Lewis–Langmuir octet theory. Examples of such molecules are SF_6, PF_5, and XeF_6 whose molecular orbitals are indicated schematically in Figure 1. In all these "orbitally deficient" molecules electrons must fill high-lying nonbonding orbitals which are located solely on the ligand atoms. This is the reason why the bonds in these molecules are weaker than in their lower valence analogs. The molecular bonding arises from the splitting between the bonding orbitals and the nonbonding orbitals and this requires the delocalization of electron charge from the central atom toward the ligands and hence electronegative ligands and an electropositive central atom.[1,8,9] Multicenter bonding does *not* occur universally but only when the nature of the different atoms is such as to satisfy these criteria.

The role played by the central atom s electrons in bonding such systems can be seen by examining Figure 1 in which all non-s-mixing electrons are indicated by filled circles on the left-hand side of the individual diagrams. If there are insufficient p electrons in the ground configuration of the central atom to provide the necessary two electrons per bond as in SF_6 and PF_5, then a p-orbital bonding description with the atomic s electrons nonmixing has an *unoccupied* nonbonding orbital (which can be taken as the symmetric

(2) F. A. Gianturco, C. Guidotti, U. Lamanna, and R. Moccia, *Chem. Phys. Lett.*, **10**, 269 (1971).
(3) H. Johansen, *ibid.*, **11**, 466 (1971).
(4) B. Roos, cited in ref 2.
(5) R. Hoffmann, J. M. Howell, and E. L. Muetterties, *J. Amer. Chem. Soc.*, to be published.
(6) A. Rauk, L. C. Allen, and K. Mislow, *ibid.*, to be published.
(7) D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **47**, 158 (1967). See also J. B. Florey and L. C. Cusachs, *J. Amer. Chem. Soc.*, to be published. These authors have reached essentially the same conclusion regarding the relative unimportance of d orbitals.[7a]
(7a) NOTE ADDED IN PROOF For some detailed calculations showing explicitly the nonbonding orbitals and the role of d orbitals in accord with the views expressed here, see R. D. Brown and J. B. Peel, *Aust. J. Chem.*, **21**, 2589, 2605, 2617 (1968).
(8) K. S. Pitzer, *Science*, **139**, 414 (1963).
(9) J. I. Musher, *ibid.*, **141**, 736 (1963). The essential neglect of d orbitals was first discussed in the theoretical sequel to this paper entitled "Nonorthogonal Hybrid Atomic Orbitals," unpublished, 1963.