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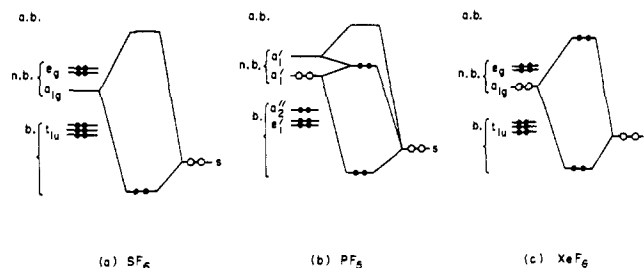

Figure 1. Molecular orbital diagrams for the σ orbitals of (a) SF_6, (b) PF_5, and (c) XeF_6 showing the occurrence of nonbonding orbitals and the mixing of the atomic s orbital with the ligand nonbonding orbitals. Filled-in circles indicate electrons in the final bonding scheme while open circles indicate 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.

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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 highlying 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.

ligand orbital shown in Figures 1a and 1b). Clearly the molecular energy will be lowered by having the atomic s orbital mix with the symmetric nonbonding orbital or orbitals so that the electrons in open circles occupy the resulting bonding and nonbonding orbitals. However, even the *qualitative* nature of the bonding depends on the details, for the orbitals can mix weakly and give essentially no bonding or strongly and make a critical contribution to the molecular stability.[1]

On the other hand, XeF_6 which is approximately octahedral (or IF_5 or SF_4 of lower symmetries) has all its nonbonding orbitals occupied before any s mixing takes place. Hence the s mixing cannot change the center of gravity of the orbital energies and can only give rise to higher order effects. There is thus a radical difference between the two types of hypervalent molecules. A MO argument which mixes orbitals of the same symmetry species indiscriminately gives a deceptive picture of the importance of s mixing and "hybridization."

This same type of MO argument also gives qualitatively incorrect inferences when the mixing of d orbitals is considered. In all of the hypervalent molecules there are nonbonding ligand orbitals of requisite symmetry to mix with central-atom d orbitals. When actual calculations are carried out, however, it is found that while the energies of the orbitals which mix are indeed lowered (by small amounts), the energies of *all* other occupied orbitals are actually raised. Table I

Table I. Highest Occupied Orbitals of SF_6[a]

	Without d	With d	Δ
$5a_{1g}$	−1.131	−1.088	+0.043
$4t_{1u}$	−0.932	−0.907	+0.025
$1t_{2g}$ (π)	−0.815	−0.816	−0.001
$3e_g$	−0.685	−0.714	−0.029
$1t_{2u}$ (π)	−0.736	−0.714	+0.022
$5t_{1u}$	−0.720	−0.697	+0.023
$1t_{1g}$ (π)	−0.690	−0.669	+0.021
E_{SCF}	−992.637	−992.931	−0.294

[a] Calculations of Roos[2] using an extended Gaussian basis with and without d orbitals. Energies are in au. The orbitals using ligand π orbitals are so indicated. The ordering is that with d orbitals included, the $3e_g$ being the only orbital whose position is shifted.

gives an example of this behavior from Roos' calculation on SF_6 and similar behavior occurs in the nonempirical calculations of Rauk, *et al.*,[6] on PH_5 and of Johansen[3] on ClO_4^-, in the Hoffmann, *et al.*,[5] extended Hückel calculation on PH_5, and was also noted by Santry and Segal[7] in their early CNDO calculations. The net lowering of the SCF energy is therefore *not* due to the lowering of the sum of the orbital energies upon mixing but to the higher order effect of modified Coulomb and exchange integrals.

Furthermore, the actual amount of energy lowering is indeed small: the calculated increments of energy due to d-orbital participation in PH_5, SF_6, and ClO_4^- are 3×10^{-4}, 3×10^{-4}, and 5×10^{-4}, respectively. This is, curiously enough, comparable to the g, h, and higher angular momentum part of the *correlation* energy of the *neon atom*[10] (and not even calculable at

(10) T. L. Barr and E. R. Davidson, *Phys. Rev. A*, 1, 644 (1970).

the present time) which is 2×10^{-4} of the *total* energy. On this basis an argument could be made for including in octahedral complexes such as SF_6 the f orbitals which will mix with the bonding t_{1u} orbitals and the g orbitals which will mix with the nonbonding a_{1g} orbital.

In any case, the quantitative results bear out the qualitative arguments of the valence-shell-electron bonding theory[1] which asserts that there is little need to introduce d orbitals into simple bonding schemes for σ-ligand orbitals. Their inclusion is neither "crucial" nor "qualitatively necessary"[11] and the role they play is little different from that of the other small corrections such as due to larger basis sets,[12] still higher angular momentum contributions, and electron correlation.

The role of ligand π electrons should not be altogether neglected even for monofunctional ligands despite the fact that bonding can be rationalized without them. As can be seen from Table I, the t_{2g} ligand π-nonbonding orbital is split off by 0.1 au from the remaining four nonbonding orbitals and thus has significant bonding character. It is felt that until we can truly assess the *magnitudes* of the π bonding, the s bonding, and the p bonding in these hypervalent molecules, all simplistic attempts to rationalize small effects, such as the "polarity rule" in phosphoranes[4,5] by either model calculations on hydrides or semiempirical calculations, should be considered premature.

(11) M. A. Ratner and J. R. Sabin, *J. Amer. Chem. Soc.*, 93, 3542 (1971).

(12) The way larger ligand basis sets actually reduce the importance of atomic d orbitals has been discussed in ref 2 and elsewhere. The interpretation of ref 2 can be criticized in that the $5a_{1g}$ orbital is 0.315 au higher than that of ref 4, while the t_{2g} orbital is only 0.049 au higher. Thus the inclusion of d orbitals gives an improvement in the t_{2g} basis that is unwarranted in view of the crudeness of the a_{1g} basis.

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Kinetics of Racemization of Amino Acids as a Function of pH

Sir:

Amino acids are known to be racemized by concentrated acid and base at elevated temperatures. However, there have been no investigations of the racemization kinetics of amino acids at intermediate pH values, except for some preliminary investigations with aspartic acid.[1,2] Of particular interest in organic geochemistry are the rates of racemization of amino acids near neutral pH. The amino acids isolated from fossil shells have been found to be partly racemized with the amount of racemization increasing with the age of the shell.[3] Recently it has been shown that the slow

(1) J. L. Bada, Ph.D. Thesis, University of California, San Diego, 1968.

(2) J. L. Bada, *Advan. Chem. Ser.*, No. 106, 309 (1971).

(3) P. E. Hare and R. M. Mitterer, *Carnegie Inst. Washington Yearb.*, 65, 362 (1967); P. E. Hare and P. H. Abelson, *ibid.*, 66, 526 (1968); P. E. Hare and R. M. Mitterer, *ibid.*, 67, 205 (1969).