TABLE I

EQUILIBRIUM PROTONATION OF PHLOROGLUCINOL AND SOME OF ITS ETHERS IN AQUEOUS PERCHLORIC ACID AT 25°

| Base | Wave length at which measurement was made, mμ | Range of acid used, wt. % | Value of $H_R'$[a] for $C_{BH^+}/C_B$ = 1.00 | No. of values of $C_{BH^+}/C_B$ | Parameters for fit to: $\log C_{BH^+}/C_B = a + bH_R'$ | | |
|---|---|---|---|---|---|---|---|
| | | | | | $a$ | $b$ | $\sigma_b$[b] |
| 1,3,5-Trimethoxybenzene | 342 | 40–58 | −7.27 | 10 | −6.06 | −0.834 | 0.034 |
| 1,3,5-Triethoxybenzene | 347 | 38–53 | −6.66 | 11 | −6.16 | − .925 | .039 |
| 3,5-Diethoxyphenol | 344 | 38–53 | −6.64 | 10 | −5.01 | − .754 | .029 |
| Phloroglucinol | 342 | 35–64 | −7.74 | 11 | −3.55 | − .459 | .015 |

[a] $H_R'$ scale constructed from $H_R$ (N. C. Deno, H. E. Berkheimer, W. L. Evans and H. J. Peterson, *J. Am. Chem. Soc.*, 81, 2344 (1959) and $a_{H_2O}$ (J. N. Pearce and A. F. Nelson, *ibid.*, 55, 3075 (1933); R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth's Scientific Publications, London, 1955, p. 504). [b] Standard deviation of mean value of $b$.

than phenol and its ethers by six powers of ten ($H_R'$ scale); the "p$K_A$'s" for anisole,[7] 1,3-dimethoxybenzene, and 1,3,5-trimethoxybenzene are −13.1, −10.9, and −7.3 ($H_R'$ scale), respectively. The introduction of successive methoxyl groups in such a series would be expected not to affect the basicity of the oxygens very much, but it should increase carbon basicity markedly. All three of these pieces of evidence indicate proton addition to carbon in phloroglucinol and its ethers, and the third indicates further that simultaneous oxygen protonation is most unlikely.

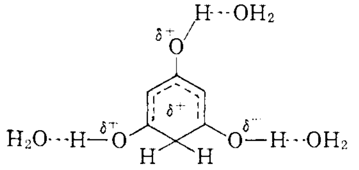
Alkylation of the phenolic groups in phloroglucinol does not affect the basicity of the aromatic ring appreciably (Table I). These substances, therefore, present a particularly useful set of bases with which to test the acidity function concept: comparison of degrees of protonation can be made in acids of the same composition. We accordingly measured indicator ratios for phloroglucinol, its triethyl and trimethyl ethers, and its diethyl ether over the same wide range of acid concentration for each compound. These data, shown in Fig. 1, can be summarized by fitting them to an expression of the type

$$\log C_{BH^+}/C_B = a + bH \qquad (1)$$

where $H$ is some acidity function and $a$ and $b$ are adjustable parameters (Table I). We employed a weighted least squares method of determining $a$ and $b$ which recognizes the fact that the error in $\log C_{BH^+}/C_B$ will be greater when $C_{BH^+}/C_B$ is very large or very small and will be a minimum when this quantity is near unity: the assigned weights were proportional to the reciprocals of the expected variances in $\log C_{BH^+}/C_B$.[10]

The data for this series of bases do not fit any established acidity function, a fact which has been corroborated for two of the substances by independent measurements in another laboratory.[5] Nor do the bases in themselves define a new acidity function: for the two bases with the most different behavior, the parameter $b$ in Equation 1—the usual measure of fit of an indicator base to an acidity function—differs by a factor of two. This is as much as the difference between the two most divergent acidity functions for uncharged bases, $H_0$ and $H_R$. This means that over the region where $C_{BH^+}/C_B$ changes from 0.1 to 10, the ratio of activity coefficients, $f_{BH^+}/f_B$, for phloroglucinol changes with composition of the medium 100 times as rapidly as the same ratio for phloroglucinol triethyl ether.

There is some reason to expect changes in activity coefficient ratios of the type $f_{BH^+}/f_B$ in concentrated acids to be the result largely of changes in $f_{BH^+}$,[4a,c,11] and the difference between phloroglucinol and its ethers can be rationalized on this basis. In protonated phloroglucinol, hydrogen-bonding interaction with the solvent through the hydroxyl groups is possible



This interaction will be stronger than in unprotonated phloroglucinol, and, of course, a similar interaction is not possible with the ethers. The result will be an increase in activity coefficient specific to those bases with hydroxyl groups which can bear positive charge in the protonated form.

We feel that this striking difference in protonation behavior between bases so similar structurally should promote a re-examination of the concept of well-defined acidity functions. We are currently engaged in doing this.

---

[10] A. J. Kresge, to be published.

[11] F. A. Long and W. F. McDevit, *Chem. Revs.*, **51**, 119 (1952); N. C. Deno and C. Perizzolo, *J. Am. Chem. Soc.*, **79**, 1345 (1957); N. C. Deno, H. E. Berkheimer, W. L. Evans and H. J. Peterson, *ibid.*, **81**, 2344 (1959).

DEPARTMENT OF CHEMISTRY
ILLINOIS INSTITUTE OF TECHNOLOGY
CHICAGO 16, ILLINOIS
UNION CARBIDE RESEARCH INSTITUTE
TARRYTOWN, NEW YORK

A. J. KRESGE
G. W. BARRY
K. R. CHARLES
Y. CHIANG

RECEIVED AUGUST 20, 1962

## CONVENTIONAL ELECTRON PAIR DESCRIPTION OF XENON COMPOUNDS

*Sir:*

Recent experiments[1] have shown the existence of $XeF_4$ and $XeF_2$, thus destroying one of the central postulates of chemical reasoning. It is important to bring to bear any theory available for explaining this phenomenon so that predictions can be made concerning probable compounds and their properties. A description has been given[2] of the quantum mechanical origin of bonding. This theory is based on our present knowledge about the detailed behavior of solutions of Schrödinger's equation.

---

[1] C. L. Chernick, *et al.*, *Science*, **138**, 136 (1962); Claassen, Selig and Malm, *J. Am. Chem. Soc.*, **84**, 3593 (1962).

[2] L. C. Allen, *Science*, **138**, 892 (1962).

Because to a zeroth approximation molecules are made out of atoms and because the largest amount of our computational experience has been with atoms, this theory treats molecular formation from the standpoint of slightly perturbed atoms. It may be noted that the theory of directed valence in carbon compounds proceeds from a similar atomic viewpoint. On the other hand we need a description which more completely reflects characteristic molecular features. There is little direct computational experience to guide us here but there is a great deal of chemical information which can be cast in quantum mechanical language and aid in establishing the geometry and other properties of molecules.[3]

To describe $XeF_4$ in this language twelve electrons are assumed to participate in molecular binding. The outer octet of xenon yields eight electrons and each fluorine supplies one. Alternatively we may start with $Xe^{+4}$ and four $F^-$ ions obtaining four electrons from the xenon ion and two from each $F^-$. Both of these are equally valid because the molecule represents a considerable distortion of its atomic constituents and we do not concern ourselves with the detailed process of molecule formation. These twelve electrons form six electron pairs. From classical electrostatic arguments the electron pairs will point toward the vertices of a regular octahedron. A fluorine atom will be located at each corner of a square centered on the xenon atom with a lone pair above and a lone pair below the plane defined by the square and each perpendicular to it. This configuration is the minimum energy way of arranging two lone pairs and four bond pairs because it minimizes the large electrostatic interaction energy between lone pairs. If we employ one-electron atomic-like basis functions of the highest possible symmetry mounted on the xenon center to form a set of directed orbitals, group theory specifies a configuration $sp^3d^2$. This merely states that basis functions of this symmetry on the xenon center plus p-like functions on the fluorine center with lobes pointed toward the xenon form convenient symmetry orbitals for $XeF_4$. Without extensive computational experiments it cannot tell us anything about the radial form of the atomic-like basis functions, their one-electron energies, the bond energies or bond lengths. However, the simple conventional nature of our picture implicitly predicts a conventional length for the xenon (analogy to iodine) fluorine bond[4]

$$1.33 + 0.64 = 1.97\text{Å}.$$

The planar structure predicted for $XeF_4$ is also suggested by the $ICl_4^-$ ion which is isoelectronic for the binding electrons and is known to be planar.[5] Preliminary Raman spectra on the solid[1] support a planar configuration. Hexafluorides are unlikely because this would require fourteen valence electrons. A general rule from chemical experience is that stable molecules with an odd number of electrons are extremely rare and so no xenon compounds with an odd number of fluorines are predicted. Identical predictions (except for the bond length) but from a more physical viewpoint were made by the perturbed atom theory.[2]

An oxygen atom can complete its outer shell by attachment to a lone pair and so an $XeF_4O$ molecule in the form of a tetragonal pyramid and an $XeF_4O_2$ molecule with tetragonal bipyramid structure potentially exist. The prediction of geometrical forms for $XeF_4O$ and $XeF_4O_2$ is easier and less uncertain in this model than in the perturbed atom theory because the asymmetry introduced by oxygen makes molecular bond predictions difficult from data based primarily on atomic calculations.[6] In our present model $XeF_3O$ is eliminated because it has an odd number of electrons.

$XeF_2$ is also known to exist[1] and molecular binding involves ten electrons—either eight from xenon and two from the fluorines or four from each. Five electron pairs are formed. The same reasoning employed for $XeF_4$ leads to a trigonal bipyramid with three triangularly arranged lone pairs in a plane and fluorines associated in bonds above and below the plane and perpendicular to the lone pairs. Orbital symmetry around xenon can be designated as $sp^3d$ or $spd^3$. $XeF_2O$, $XeF_2O_2$, $XeF_2O_3$ are all predicted with equal *a priori* probability. In place of an oxygen atom $BF_3$ or another Lewis acid might be attached in either the $XeF_2$ or $XeF_4$ series.

It is a comment on the present state of our understanding of chemical structure that neither computational nor chemical experience have yet given us enough knowledge to have made a confident *a priori* prediction of the stability of $XeF_4$ or $XeF_2$.

---

[3] N. Sidgwick and H. Powell, *Proc. Roy. Soc.* (*London*), **A176**, 153 (1940); R. Gillespie and R. Nyholm, *Quant. Rev.*, **11**, 339 (1957); "Progress in Stereochemistry," Vol. 2, Chapter 8, Academic Press, New York, N. Y., 1962); R. Gillespie, *Canad. J. Chem.*, **38**, 818 (1960).

[4] Data from L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 3rd Ed., 1960.

[5] R. C. L. Mooney, *Z. Krist.*, **98**, 377 (1938).

[6] Unfortunately there have been no *ab initio* molecular calculations that directly relate to this geometry.

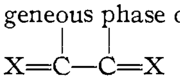
DEPARTMENT OF CHEMISTRY LELAND C. ALLEN
PRINCETON UNIVERSITY WILLIAM DEW. HORROCKS, JR.
PRINCETON, NEW JERSEY

RECEIVED OCTOBER 22, 1962

## STEREOCHEMISTRY OF METAL ADDITION TO CONJUGATED SYSTEMS. I. BENZIL

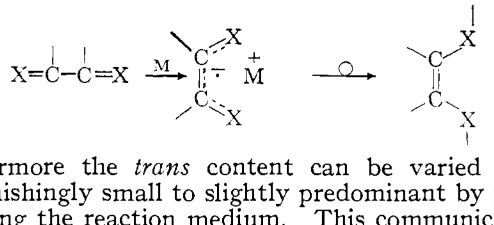
*Sir:*

We wish to report evidence that the addition of metals, either monovalent or divalent, as a heterogeneous phase or in solution, to conjugated systems



$X{=}C{-}C{=}X$

exhibits a pronounced *cis* stereochemical preference, ultimately yielding products thermodynamically rich in or exclusively composed of the less stable *cis* olefinic isomer (1). Furthermore the *trans* content can be varied from vanishingly small to slightly predominant by regulating the reaction medium. This communication submits extensive data for a system (benzil) with



(1)