to the difference in acid strength or pK_a of the acids AH and BH by eq 2, if we define an absolute acidity[7] in the

$$\log K = pK_a(\mathrm{AH}) - pK_a(\mathrm{BH}) \equiv \Delta pK_a \qquad (2)$$

gas phase by analogy with solution work, eq 3. Here

$$pK_a(\mathrm{gas}) = \Delta G°(\mathrm{gas})/2.303RT - \log [\mathrm{H_2O}] \qquad (3)$$

$\Delta G°$(gas) is the standard free-energy change for reaction 4. The pK_a(gas) for ethanol defined in this way can be

$$\mathrm{AH\ (gas) + H_2O\ (gas) \rightleftharpoons A^-\ (gas) + H_3O^+\ (gas)} \qquad (4)$$

estimated from available thermochemical data to be 154.8 ± 2.8 kcal/mol.[8] This value (as a reference) leads to values of pK_a (gas) for methanol, isopropyl alcohol, and *tert*-butyl alcohol of 155.3 ± 2.8, 153.8 ± 2.8, and ≤154.2 ± 2.8, respectively.

The extent to which the acid strength of these alcohols measured in solution truly reflects the gas-phase acidity can be appreciated from a comparison of ΔpK_a's (or standard free-energy changes for reaction 1) measured in these two phases. For example, we have shown that $pK_a(\mathrm{CH_3OH}) - pK_a(\mathrm{C_2H_5OH}) = 0.5$ and that $pK_a(\mathrm{C_2H_5OH}) - pK_a(i\text{-}\mathrm{C_3H_7OH}) = 1$ in the gas phase at 300°K. Solution measurements indicate that these values of ΔpK_a are -2 and 0, respectively, in benzene at room temperature.[9] Thus both the absolute magnitude and the sign of ΔpK_a (or $\Delta G°$ for reaction 1), *i.e.*, the difference in acid strength and the order of acidity, can change in going from the gas phase to, in this case, benzene solution.

The gas-phase acidity order determined in these experiments is entirely consistent with the acidity sequence first reported by Brauman and Blair,[2] and the values of ΔpK_a (gas), *i.e.*, $\Delta G°_{300}$, reported here are a quantitative measure of the intrinsic structure–reactivity patterns discussed by them. Gas-phase values for the standard free-energy change in proton transfer reactions of type 1 and solution values for the same quantity can complement each other in the determination of thermochemical quantities, such as free energies of solvation of anions, which are usually inaccessible to solution studies alone. Conversely, of course, a knowledge of the standard free-energy change in proton transfer reactions proceeding in the gas phase and certain free energies of solvation can be valuable in predicting the relative acidity of two acids in solution.

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(7) Water is taken as the standard base and 55.5 mol/l. is adopted as the basic quantity of water.

(8) We calculate a value of $\Delta G°_{300} = 216 \pm 4$ kcal/mol for the reaction $\mathrm{C_2H_5OH\ (gas) + H_2O\ (gas) \rightleftarrows C_2H_5O^-\ (gas) + H_3O^+\ (gas)}$. The proton affinity of H_2O was taken to be 164 ± 4 kcal/mol: J. Long and B. Munson, *J. Chem. Phys.*, **53**, 1356 (1970). The electron affinity of C_2H_5O was taken to be 38.7 kcal/mol: J. H. Williams and W. H. Hamill, *ibid.*, **49**, 4467 (1968). $D(\mathrm{C_2H_5OH})$ was taken to be 104.3 kcal/mol: S. W. Benson and R. Shaw, *Advan. Chem. Ser.*, **No. 75**, 288 (1968). The standard entropies of H_3O^+ and $C_2H_5O^-$ were set equal to those of their isoelectronic species NH_3 and C_2H_5F: JANAF Thermochemical Tables, Dow Chemical Co., Midland, Mich., 1965 and 1966.

(9) W. K. McEwen, *J. Amer. Chem. Soc.*, **58**, 1124 (1936).

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Walsh's Rules, Closed Shells, and Localized Electron Models

Sir:

Takahata, Schnuelle, and Parr[1] have recently formulated Walsh's rules[2] in a useful way, allowing quantitative prediction of bond angles. Their model (called TSP below) permits predictions for short-lived species, excited states, and species containing unpaired electrons, and thus may be a valuable addition to our predictive tools. Study of its relationship to other models thus would appear profitable. Walsh's predictions have previously been shown[3] to match closely those of the valence-shell-electron-pair-repulsion[4] (VSEPR) and other electron-domain models proposed by Gillespie,[4] Linnett,[5] and Bent.[6] We propose to indicate that where comparison is possible TSP is qualitatively very similar to other localized-electron models, and to present comparative bond angle calculations using a VSEPR-type model.

The TSP model assumes a molecule AH_mB_n in which the other atoms are bonded to central atom A. The valence shells of the H and B atoms are filled, producing anions, and the remaining electrons are assigned to sp and $p\pi$[7] orbitals on A, the hybridization being justified as a second-order Jahn–Teller effect.[8] The hybrids must correspond to the molecular symmetry, and $p\sigma$[7] orbitals with respect to ligand ion positions are used last. The equilibrium geometry is then found by minimizing the repulsions between the ions and the hybrid orbitals.

In a molecule described by a single localized paired-electron structure, the TSP can be matched to the VSEPR model as follows: one electron pair on each ligand ion is visualized as a σ-bond pair to A, and a filled $p\pi$ pair is combined with the sp hybrid to form two symmetry-related localized lone pairs. H and B ions repel lone pairs in the TSP just as do bond pairs in the VSEPR. Repulsions involving lone pairs are stronger than those between ions in the TSP model because lone pairs are at a much shorter radius. In the VSEPR model, space requirement in the valence shell of atom A is less for a bond pair than for a lone pair, and decreases as the electronegativity of the atom B increases. Thus, in either model, lone pairs preempt larger solid angles about A than do bonds. In a molecule such as O_3, where resonance between two or more Lewis structures would be required, the equivalence can still be

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(1) Y. Takahata, G. W. Schnuelle, and R. G. Parr, *J. Amer. Chem. Soc.*, **93**, 784 (1971).

(2) A. D. Walsh, *J. Chem. Soc.*, 2260 (1953), and eight consecutive succeeding articles.

(3) H. B. Thompson, *Inorg. Chem.*, **7**, 604 (1968).

(4) R. J. Gillespie, *J. Amer. Chem. Soc.*, **82**, 5978 (1960); *J. Chem. Educ.*, **40**, 295 (1963). For development of the VSEPR approach, see N. V. Sidgwick and H. M. Powell, *Proc. Roy. Soc.*, *Ser. A*, **176**, 153 (1940); J. E. Lennard-Jones and J. A. Pople, *ibid.*, *Ser. A*, **202**, 166 (1950); R. J. Gillespie and R. S. Nyholm, *Quart. Rev.*, *Chem. Soc.*, **11**, 339 (1957).

(5) J. W. Linnett, *J. Amer. Chem. Soc.*, **83**, 2643 (1961); "The Electronic Structure of Molecules. A New Approach," Wiley, New York, N. Y., 1964.

(6) H. A. Bent, *Fortschr. Chem. Forsch.*, **14**, 1 (1970); *J. Chem. Educ.*, **45**, 768 (1968); 40, 446, 523 (1963).

(7) These specifications are sufficient for the triatomic species considered to date, but may require clarification when applied, for example, to ClF_3 or SF_4. The author is grateful to Robert G. Parr and Gary W. Schnuelle for discussions regarding their model.

(8) L. S. Bartell, *J. Chem. Educ.*, **45**, 754 (1968); R. G. Pearson, *J. Chem. Phys.*, **52**, 2167 (1970); *J. Amer. Chem. Soc.*, **91**, 4947 (1969).

demonstrated by employing a σ–π separation, modifying the VSEPR treatment.[3]

To compare quantitative predictions, the following VSEPR model was examined: bonded and lone electron pairs were placed on a sphere and were assumed to repel one another according to a potential of the form $1/r^n$. Appropriate values of n have been considered elsewhere.[9] Calculations using $n = 2$ and 4 appear in Table I. Mutual bond-pair repulsions were weighted by a factor of 0.5, lone-pair repulsions by 1.0, and bond-pair–lone-pair repulsions by the geometric mean, 0.7. A single unpaired electron was given half the weight of a pair. These factors represent the lessened presence of bonding electrons in the valence shell, as assumed in VSEPR discussions.[4] For $^2A_1$ NH_2 and $^3B_1$ CH_2 a pπ orbital was used as in the TSP calculations. For O_3, two C_s symmetry models gave predicted bond angles differing by less than a degree. In one model, the double bond was represented by two coincident pairs. Alternatively, the two pairs of a bent-bond double bond were placed above and below the molecular plane.

Table I. Bond Angle Predictions from Various Models

Symmetry[a]	Calcd angle[a] $n = 2$	$n = 4$	Exptl[b] angle	Calcd TSP	Molecule
$^2A_1$	128	126	131	118	BH_2
			119	117	AlH_2
$^1A_1$	112	114	101	99	SiF_2
			102	100	CH_2
$^3B_1$	128	126	136[c]	120	CH_2
$^2A_1$	128	126	144	120	NH_2
			123	118	PH_2
$^1A_1$	103	104	105	102	H_2O
			92	99	H_2S
			104	107	OF_2
$^1A_1$, $^1A'$	120	118	117	128	O_3
			120	120	SO_2
			118	122	SSO
$^1A_1$	106	107	108		NH_3
			93		PH_3
$^1A_1$	85	86	87[d]		ClF_3
			86[d]		BrF_3

[a] Given for each new configuration. [b] Same sources as ref 1 unless otherwise indicated. [c] G. Herzberg and J. W. C. Johns, *J. Chem. Phys.*, **54**, 2277 (1971). [d] L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, **No. 11**, M87 (1958); **No. 18**, M49s (1965).

This is to our knowledge the first attempt to apply a quantitative VSEPR-type model to a variety of molecules.[10] No claim is made that the form is optimal—for example, ligand electronegativity was ignored. However, the model gives encouraging results, comparable to those from the TSP. Neither model handles well the frequent sharp difference between second-shell and third-shell valence angles; the TSP angle change is in the right direction, but in each case is much too small. The small dependence of the VSEPR predictions on n is encouraging, since the best function is probably not a single reciprocal power.

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[9] H. B. Thompson and L. S. Bartell, *Inorg. Chem.*, 7, 488 (1968); W. J. Adams, H. B. Thompson, and L. S. Bartell, *J. Chem. Phys.*, **53**, 4040 (1970).

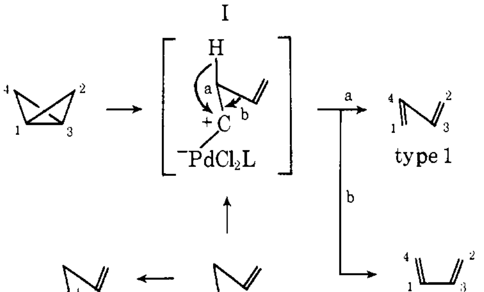
[10] See, however, A. W. Searcy, *ibid.*, **28**, 1237 (1958), for an electrostatic model using different weighting for differing electron pairs. Recent electron-domain models (see ref 3–6) have assumed that localized pairs are separated primarily by exclusion-principle considerations. Searcy determined empirically a different weighting for each type of ligand, and for a second-period central atom as opposed to a third- or higher period atom. With this flexibility, Searcy duplicated well a variety of bond angles.

Silver(I)-Catalyzed Rearrangement of Bicyclobutanes. Some Aspects of the Mechanism. I

Sir:

Numerous reports have appeared recently concerning the rearrangement of the bicyclobutane system promoted by metals of the second and third transition series, in particular, Rh(I), Pd(II), and Ag(I).[1] Three aspects of this rearrangement soon became apparent: (i) various alkyl-substituted bicyclobutanes are isomerized to butadienes in almost all cases investigated; (ii) products can be classified into two groups, those (type 1) resulting from a formal C-1,2 and C-1,3 cleavage of bicyclobutanes and those (type 2) from a C-1,2 and C-3,4 bond cleavage; and (iii) the distribution between the two types of products is very sensitive to the positions of alkyl substituents on the starting material and the kind of metal catalyst employed in the reaction. In the case of Pd(II) we proposed the intermediacy of a metal complex of structure I[1b,2] which led to the type 1 and presumably also to the type 2 product. However, we avoided proposing a similar Ag(I) complex II[3] as an intermediate common to all reactions. In this communication we present experimental results which are consistent with our earlier proposals for the Pd(II)–bicyclobutane reaction but suggest that intermediate II may not necessarily be involved in several Ag(I)-catalyzed reactions, in particular, those producing the type 2 product.

Scheme I



Recent studies[4] have indicated that reactions of diazoalkanes with transition metals [including Ag(I)] lead to the formation of complexes consisting of the

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(1) For Rh(I): (a) P. G. Gassman, T. J. Atkins, and F. J. Williams, *J. Amer. Chem. Soc.*, **93**, 1812 (1971), and references quoted therein. For Pd(II): (b) M. Sakai, H. Yamaguchi, and S. Masamune, *Chem. Commun.*, 486 (1971), and references quoted therein. For Ag(I): (c) L. A. Paquette, R. P. Henzel, and S. E. Wilson, *J. Amer. Chem. Soc.*, **93**, 2335 (1971), and (d) M. Sakai, H. Yamaguchi, H. H. Westberg, and S. Masamune, *ibid.*, **93**, 1043 (1971), and references therein.

(2) In ref 1a, a Rh complex similar to I is described, using two resonance structures.

(3) The argentocarbonium ion proposed by Paquette, *et al.*,[1c] is essentially the representation of an extreme resonance form of the formal Ag(I)–carbene complex.

(4) W. Kirmse and K. Horn, *Chem. Ber.*, **100**, 2698 (1967); W. R. Moser, *J. Amer. Chem. Soc.*, **91**, 1135 (1969).