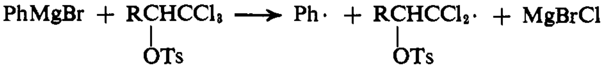
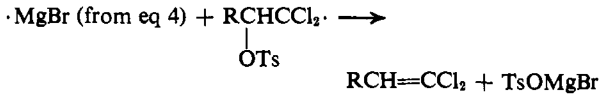
products were isolated by distillation or glpc and identified by ir, nmr, and elemental analyses.

The mechanism of the reaction is puzzling; we tentatively propose the following

 (1)

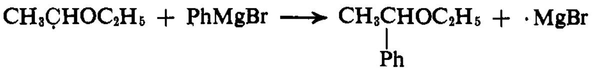
$$PhMgBr + RCH(OTs)CCl_3 \longrightarrow Ph\cdot + RCH(OTs)CCl_2\cdot + MgBrCl \quad (1)$$

 (2)

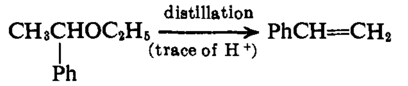
$$\cdot MgBr\ (\text{from eq 4}) + RCH(OTs)CCl_2\cdot \longrightarrow RCH{=}CCl_2 + TsOMgBr \quad (2)$$

and the observed by-products arise from

$$Ph\cdot + C_2H_5OC_2H_5 \longrightarrow C_6H_6 + CH_3\dot{C}HOC_2H_5 \quad (3)$$

 (4)

$$CH_3\dot{C}HOC_2H_5 + PhMgBr \longrightarrow CH_3CH(Ph)OC_2H_5 + \cdot MgBr \quad (4)$$

 (5)

$$CH_3CH(Ph)OC_2H_5 \xrightarrow[\text{(trace of } H^+)]{\text{distillation}} PhCH{=}CH_2 \quad (5)$$

Most Grignard reactions occur by a polar, "ionic" mechanism (although ionic dissociation is not a prerequisite) but certain radical reactions are well known.[3] The nature of the by-products in the case of the reaction of the Grignard reagent with the tosylate of the (trichloromethyl)carbinol strongly suggests a free-radical mechanism. A homolytic cleavage of the Grignard reagent is required to obtain the radicals to form the $\alpha$-substituted diethyl ethers. Two ·MgBr radicals serve as reducing agents to supply two electrons to the tosylate, probably through the d orbitals of the chlorine atoms, which causes the tosylate anion to be expelled. With benzylmagnesium bromide, the relatively stable benzyl radical[4] formed in eq 1 reacts with the Grignard reagent to form bibenzyl rather than attacking the solvent as in the other cases (eq 3).

The carbinols and their tosylates are easily prepared by standard methods, and the subsequent reactions of their tosylates with Grignard reagents provide an attractive synthetic route to the dichloro olefins.

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[3] Reference 1, pp 116 and 138.

[4] E. S. Huyser, "Free Radical Chain Reactions," Wiley-Interscience, New York, N. Y., 1970, p 69.

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## A Standard Acidity Scale. The p$K_a$ of Alcohols in the Gas Phase

*Sir:*

It has been realized for some time that the observed acid strength of uncharged acids in the condensed phase can be a strong function of the nature of the solvent. This has led to a number of acidity scales and acidity functions all of which are highly dependent on the specific solvent system.[1] Since the exact nature of solvation effects is quite complex and not generally understood it seems natural to avoid solvation when defining an acidity scale and adopt the acid strength in the gas phase as a standard. Recent experimental innovations have led to the first determinations of orders of acidity in the gas phase.[2,3] We report here the first quantitative measurements of differences in gas-phase acidities of uncharged acids which suggest that the adoption of the gas-phase acidity as a standard acidity may now indeed become practicable.

The technique employed for these measurements was the flowing afterglow technique[4] which has recently been applied to the study of negative ion-molecule reactions of interest in organic chemistry. Rate constants were measured for both the forward and reverse direction of proton transfer in reactions of type 1 proceeding in the gas phase at 300°K. The experimental results are summarized in Tables I and II. Proton transfer between the selected alcohol molecules and alkoxide ions was observed to be quite rapid, $k \geq 5 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$, in both directions in all three cases (Table I). The values for the equilibrium constants, $K$, listed in Table I were deduced[5] from the experimental data recorded in a study of the tendency of acetylene to transfer a proton to the alkoxide ions (Table II).[6]

$$A^- + BH \rightleftarrows B^- + AH \quad (1)$$

**Table I.** Thermochemical Data for the Acid-Base Equilibria between Selected Alcohols in the Gas Phase at 300°K

| Acid-base equilibrium | $K$ | $-\Delta G°_{300}$, kcal/mol | $\Delta pK_a$ |
|---|---|---|---|
| $CH_3O^- + C_2H_5OH \rightleftarrows C_2H_5O^- + CH_3OH$ | 3 | 0.7 | 0.5 |
| $C_2H_5O^- + i\text{-}C_3H_7OH \rightleftarrows i\text{-}C_3H_7O^- + C_2H_5OH$ | $1 \times 10$ | 1.4 | 1 |
| $i\text{-}C_3H_7O^- + tert\text{-}C_4H_9OH \rightleftarrows tert\text{-}C_4H_9O^- + i\text{-}C_3H_7OH$ | $\geq 0.3$ | $\geq -0.7$ | $\geq -0.5$ |

**Table II.** Rate Constants for the Proton Transfer Reactions between Alkoxide Ions and Acetylene in the Gas Phase at 300°K

| Alkoxide ion | $k_f$ ($\times 10^9$ cm$^3$ molecule$^{-1}$ sec$^{-1}$) | $k_r$ | $K \times 10^{-1}$ | $-\Delta G°_{300}$, kcal/mol | $\Delta pK_a$ |
|---|---|---|---|---|---|
| $CH_3O^-$ | 1.3 | 0.05 | 3 | 2.1 | 1.5 |
| $C_2H_5O^-$ | 1.1 | 0.1 | 1 | 1.4 | 1 |
| $i\text{-}C_3H_7O^-$ | 0.52 | 0.5 | 0.1 | 0 | 0 |
| $tert\text{-}C_4H_9O^-$ | 0.16 | $\geq 0.05$ | $\leq 0.3$ | $\leq 0.7$ | $\leq 0.5$ |

The thermodynamic equilibrium constant, $K$, for reaction 1 proceeding in the gas phase can be related

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[1] See, for example, D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, Chapter 1.

[2] J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **92**, 5986 (1970).

[3] D. K. Bohme and L. B. Young, *ibid.*, **92**, 3301 (1970).

[4] E. E. Ferguson, *Advan. Electron. Electron Phys.*, 24, 1 (1968); E. E. Ferguson, F. C. Fehsenfeld, and A. L. Schmeltekopf, *Advan. At. Mol. Phys.*, **5**, 1 (1969). See ref 3 for details concerning the application of this technique to the organic chemistry of negative ions in the gas phase.

[5] The ratio of the rate constant for the forward direction of proton transfer, $k_f$, to the rate constant for the reverse direction, $k_r$, was taken to be equal to the thermodynamic equilibrium constant since the energy distributions of the respective reactants are expected to be Maxwell-Boltzmann. The standard free-energy change, $\Delta G°$, can then be computed by employing the relation $\Delta G° = -RT \ln K$.

[6] For information regarding the generation of alkoxy anions in the gas phase see: D. K. Bohme and L. B. Young, *J. Amer. Chem. Soc.*, **92**, 7354 (1970).

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

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

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

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

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

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

estimated from available thermochemical data to be 154.8 ± 2.8 kcal/mol.[8] This value (as a reference) leads to values of p$K_a$ (gas) for methanol, isopropyl alcohol, and *tert*-butyl alcohol of 155.3 ± 2.8, 153.8 ± 2.8, and $\leq$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 $\Delta$p$K_a$'s (or standard free-energy changes for reaction 1) measured in these two phases. For example, we have shown that p$K_a$($CH_3OH$) − p$K_a$($C_2H_5OH$) = 0.5 and that p$K_a$ ($C_2H_5OH$) − p$K_a$(*i*-$C_3H_7OH$) = 1 in the gas phase at 300°K. Solution measurements indicate that these values of $\Delta$p$K_a$ are −2 and 0, respectively, in benzene at room temperature.[9] Thus both the absolute magnitude and the sign of $\Delta$p$K_a$ (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 $\Delta$p$K_a$ (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 ± 4 kcal/mol for the reaction $C_2H_5OH$ (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($C_2H_5OH$) 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 $\sigma$-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).