Gas-Phase Acidities of Binary Hydrides

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Abstract: The relative gas-phase acidities of a number of binary hydrides have been determined. The order $H_2S > AsH_3 > PH_3 > SiH_4 > H_2O > NH_3 > CH_4$ allows acidities to be analyzed in terms of the position of the central atom in the periodic table.

The general problem of relating structure and reactivity in ionic reactions using data obtained from solution studies is substantially complicated by solvation effects. In our previous ion cyclotron resonance (icr) studies of acid–base reactions in the gas phase,[2–4] we have noted, among other things, reversals in the acidity order of alcohols[2] between gas and solution phase and other rather startling discrepancies between solution and gas-phase observations (*viz.*, toluene and propylene are stronger acids than water). These changes and "unusual" orders appear to result from the extremely high heats of solvation of the ions, differences in which often obscure the modest intrinsic differences in energy due to the unsolvated ions themselves. This can be attributed in part to the great endothermicity of gas-phase dissociation as compared with solution. For example, $\Delta H° = +333$ kcal/mol for HCl dissociation in the gas phase, -16 kcal/mol in water.[5]

Simple binary hydrides, XH_n, are a particularly attractive category of molecules to examine with respect to gas-phase acidities, since one might hope to see trends corresponding to classification in the periodic table and to compare, then, the effects of structure and solvation on the relative acidities. The binary hydrides constitute the simplest class and comprise the most fundamental series of acids, both in terms of major, but predictable, structural changes, and in terms of accessible experimental tests of quantum mechanical calculations. For example, knowledge of anion stabilities is crucial in evaluating electron correlation energies.

Indeed, acidities of binary hydrides have been the subject of substantial thought, and numerous books[6] and articles[5,7] discuss this topic as a guide to periodic trends. These analyses have depended substantially on solution data, since no other were available. That the area is still in need of research is clear, since only recently have the relative acidities of water and ammonia been determined.[3] Also, results of calculations and certain data can be interpreted as being at variance with our experimental results as well as with expected periodic trends.[8]

In this paper, we report on the experimental determination, by icr, of relative acidities of some binary hydrides, by studying the preferred direction of proton transfer in reactions represented by eq 1. We also present sufficient data to make clear the periodic trends in acidities and the underlying trends in other, fundamental thermochemical quantities which influence acidity.

$$AH_n + BH_{m-1}^- \rightleftharpoons AH_{n-1}^- + BH_m \qquad (1)$$

Results

The method utilized to ascertain relative acidities was that reported previously.[9] The preferred direction for proton transfer was probed by icr double resonance, by pressure dependence studies[10] in which ion abundance was monitored as a function of neutral concentration, and by intensity *vs.* time studies using a trapped-ion analyzer cell.[11] The icr double-resonance experiments were carried out in both directions to ensure that there were no inconsistencies.

Some of the pertinent reactions examined[12] are listed in Table I. The reactions listed can be used to determine a relative acidity order of $H_2S > AsH_3 > PH_3 > SiH_4 > H_2O > NH_3 > CH_4$. The relative acidity of methane can only be inferred from the observations that while NH_2^- can abstract a proton from CH_3Cl and other halogenated alkanes, no proton abstraction could be observed from isobutane. Assuming that isobutane and methane have comparable acidities, we deduce the order of acidities to be $CH_3Cl > NH_3 > CH_4$.

We have recently determined[13] the electron affinities of $PH_2\cdot$ and $NH_2\cdot$. These data, together with *reliable* electron affinities and bond dissociation energies previously determined, allow us to evaluate $\Delta H°$ for certain binary hydride heterolytic dissociations (see later discussion). These are (kcal/mol) HI, 314; HBr,

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[2] (a) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **92**, 5986 (1970); (b) *ibid.*, 90, 6561 (1968).

[3] J. I. Brauman and L. K. Blair, *ibid.*, **91**, 2126 (1969); **93**, 3911 (1971); J. I. Brauman, J. M. Riveros, and L. K. Blair, *ibid.*, **93**, 3914 (1971).

[4] J. I. Brauman and L. K. Blair, *ibid.*, 90, 5636 (1968).

[5] J. C. McCoubrey, *Trans. Faraday Soc.*, **51**, 743 (1955). Some numbers used in this paper have been corrected to correspond with more recent values.

[6] For example, T. Moeller, "Inorganic Chemistry," Wiley, New York, N. Y., 1952, p 318; J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962, p 58.

[7] For example, L. Pauling, *J. Chem. Educ.*, **33**, 16 (1956).

[8] See, for example, C. D. Ritchie and H. F. King, *J. Amer. Chem. Soc.*, 90, 838 (1968), which includes both calculations and an analysis of some experimental data.

[9] See ref 2–4 for pertinent references and details, especially ref 2a.

[10] D. Holtz, J. L. Beauchamp, and J. R. Eyler, *J. Amer. Chem. Soc.*, 92, 7045 (1970).

[11] R. T. McIver, Jr., *Rev. Sci. Instrum.*, 41, 555 (1970). The cell allows ions to be trapped for times longer than 100 msec, thus permitting them to undergo many collisions and to approach thermal equilibrium.

[12] Some of these reactions have been reported previously.[2,3,10]

[13] K. C. Smyth, R. T. McIver, Jr., J. I. Brauman, and R. W. Wallace, *J. Chem. Phys.*, 54, 2758 (1971); J. I. Brauman and K. C. Smyth, *J. Amer. Chem. Soc.*, **91**, 7778 (1969).

Table I. Reactions of Binary Hydrides

No.	Reaction	Result[a]	Method[b]
1	$NH_2^- + (CH_3)_3CH = NH_3 + (CH_3)_3C^-$	No product ion observed	
2	$NH_2^- + ClCH_3 = NH_3 + ClCH_2^-$	$\rightarrow$	DR
3	$NH_2^- + H_2O = NH_3 + OH^-$	$\overset{\rightarrow}{\nleftarrow}$	DR
4	$NH_2^- + SiH_4 = NH_3 + SiH_3^-$	$\rightarrow$	T
5	$NH_2^- + PH_3 = NH_3 + PH_2^-$	$\overset{\rightarrow}{\nleftarrow}$	DR, P
6	$OH^- + SiH_4 = H_2O + SiH_3^-$	$\overset{\rightarrow}{\nleftarrow}$	DR, T
7	$OH^- + PH_3 = H_2O + PH_2^-$	$\overset{\rightarrow}{\nleftarrow}$	DR, P
8	$OH^- + H_2S = H_2O + SH^-$	$\rightarrow$	DR
9	$n\text{-}C_4H_9O^- + SiH_4 = n\text{-}C_4H_9OH + SiH_3^-$	$\rightarrow$	P[c]
10	$SiH_3^- + CH_4 = SiH_4 + CH_3^-$	No product ion observed	
11	$SiH_3^- + PH_3 = SiH_4 + PH_2^-$	$\overset{\rightarrow}{\nleftarrow}$	DR, P, T
12	$SiH_3^- + H_2S = SiH_4 + SH^-$	$\overset{\rightarrow}{\nleftarrow}$	DR, T
13	$PH_2^- + AsH_3 = PH_3 + AsH_2^-$	$\overset{\rightarrow}{\nleftarrow}$	DR, P, T
14	$PH_2^- + H_2S = PH_3 + SH^-$	$\overset{\rightarrow}{\nleftarrow}$	DR, P
15	$AsH_2^- + H_2S = AsH_3 + SH^-$	$\overset{\rightarrow}{\nleftarrow}$	P, T
16	$Cl^- + HBr = HCl + Br^-$	$\overset{\rightarrow}{\nleftarrow}$	DR

[a] $\rightarrow$ indicates that the reactants were present and the reaction proceeded to the right, as evidenced by pressure dependence and/or double resonance. $\nleftarrow$ indicates that the reactants were present but no reaction to the left could be detected by double resonance. The absence of an arrow indicates that the reaction was not studied in that direction. [b] DR = double resonance, P = pressure dependence, T = intensity *vs.* time. [c] Reactions with more basic alkoxides such as CH_3O^-, $C_2H_5O^-$, etc., were also examined.

324; HCl, 333; H_2S, 350; PH_3, 364; HF, 370; H_2O, 390; and NH_3, 407.

Together with the direct relative acidity determinations, this allows us to develop the gas-phase periodic trends indicated below. Acidities in the right-hand part of the periodic table thus appear to increase as one moves left to right along a given row or down a given column.

$$\begin{array}{ccccccc}
CH_4 & < & NH_3 & < & H_2O & < & HF \\
\wedge & & \wedge & & \wedge & & \wedge \\
SiH_4 & < & PH_3 & < & H_2S & < & HCl \\
 & & \wedge & & & & \wedge \\
 & & AsH_3 & & < & & HBr \\
 & & & & & & \wedge \\
 & & & & & & HI
\end{array}$$

Discussion

We have previously[2-5,14] found it convenient to analyze acidities in terms of the thermochemical cycle, eq 2, where $DH°$ is the bond dissociation energy of AH, EA is the electron affinity of $A\cdot$, and IP is the ionization potential of $H\cdot$. In comparing a pair of acids, it is often possible to predict the direction of change of both $DH°$ and EA. However, it is more difficult to predict the acidity order, since an increase in EA is often associated with an increase in $DH°$. This relationship has been recognized for many years and is, for example, at the heart of the Pauling electronegativity definition.[15] Thus, increasing EA may or may not increase acidity, depending on the change in $DH°$. As an example, acetylene and HF are both stronger acids than H_2O in spite of having greater $DH°$ (electron affinity is more important), while HBr is a stronger acid than HCl in spite of its lower EA ($DH°$ is more important).

$$\begin{array}{llr}
AH \longrightarrow A\cdot + H\cdot & D & (2a) \\
A\cdot + e^- \longrightarrow A^- & -EA & (2b) \\
\underline{H\cdot \longrightarrow H^+ + e^-} & \underline{IP} & (2c) \\
AH \longrightarrow A^- + H^+ & \Delta H° & (2d)
\end{array}$$

There are, however, underlying trends in the bond strengths and electron affinities themselves which are of value in tracing the acidity trends. These are seen in Table II. Most of the data are given to the nearest kilocalorie; some bond energies can only be estimated. It is clear that the controlling feature in determining relative acidities is that electron affinities are more important as one progresses along a row, and bond energies are more important as one moves down a column. Some of these trends have been noted previously.[3,10] This can easily be understood in simple terms with the help of molecular orbital theory.

Table II. Bond Dissociation Energies and Electron Affinities

	$DH°$	EA		$DH°$	EA
CH_4	104[a]		H_2S	90[a]	53[j]
NH_3	110[b]	17[c]	HCl	103[e]	83[f]
H_2O	119[a]	42[d]	AsH_3	*k*	29.3[l]
HF	136[e]	80[f]	HBr	88[e]	78[f]
SiH_4	80[g]	*h*	HI	71[e]	71[f]
PH_3	80[i]	28.8[c]			

[a] J. A. Kerr, *Chem. Rev.*, **66,** 465 (1966). [b] R. K. Solly, N. A. Gac, D. M. Golden, and S. W. Benson, submitted for publication. [c] K. C. Smyth, R. T. McIver, Jr., J. I. Brauman, and R. W. Wallace, *J. Chem. Phys.*, **54,** 2758 (1971). [d] L. M. Branscomb, *Phys. Rev.*, **148,** 11 (1966). [e] S. W. Benson, *J. Chem. Educ.*, **42,** 502 (1965). [f] R. S. Berry and C. W. Reimann, *J. Chem. Phys.*, **38,** 1540 (1963). [g] B. deB. Darwent, "Bond Dissociation Energies in Simple Molecules," NSRDS-NBS 31, U. S. Government Printing Office, Washington, D. C., 1970. [h] The electron affinity of $SiH_3\cdot$ can be estimated at 20–29 kcal/mol by using the EA of $C_4H_9O\cdot$ [J. M. Williams and W. H. Hamill, *J. Chem. Phys.*, **49,** 4467 (1968)] to estimate the absolute acidity of C_4H_9OH and the result that the acidity of SiH_4 lies between C_4H_9OH and PH_3. [i] Computed from the appearance potential at 2.2 eV for $PH_3 \rightarrow PH_2^- + H\cdot$ by M. Halmann and I. Platzner, *J. Phys. Chem.*, **73,** 4376 (1969), and the electron affinity of $PH_2\cdot$. [j] B. Steiner, *J. Chem. Phys.*, **49,** 5097 (1968). [k] The bond dissociation energy in AsH_3 is not known. The average bond energy is computed to be 71 kcal/mol from heats of formation of H, As, and AsH_3: D. D. Wagman, *et al.*, "Selected Values of Chemical Thermodynamic Properties," NBS 270-3, U. S. Government Printing Office, Washington, D. C., 1968. [l] K. C. Smyth, determined by photodetachment, manuscript in preparation.

Simple perturbation arguments[16] suggest that when an A–H bond MO, ψ, is constructed from atomic orbitals φ_A and φ_H, the stabilization of ψ relative to φ_A will be greatest when the orbitals φ_A and φ_H have comparable energies. As φ_A becomes progressively more electronegative (and thus more stable) the mixing coefficient becomes smaller and ψ approaches φ_A in energy, as shown in Figure 1.

More formally, the 2 × 2 secular equations (neglecting overlap) lead to the result for the energy, E_ψ, of of the MO ψ

$$E_\psi = E_A + (1/2)[\Delta - (\Delta^2 + 4V^2)^{1/2}] \qquad (3a)$$

where $\Delta \equiv E_H - E_A$ is the difference between the orbital energies of φ_H and φ_A, and V is the strength of the perturbative interaction.[17]

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(14) A. Streitwieser, Jr., and J. H. Hammons, *Progr. Phys. Org. Chem.*, 3, 41 (1965).

(15) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, Chapter 3.

(16) See R. Hoffmann, *Accounts Chem. Res.*, 4, 1 (1971), for a recent application of perturbation theory and pertinent references.

(17) To first order, when V is small compared to Δ, $E_\psi = E_A - (V^2/\Delta)$; $2E_A - 2E_\psi = 2V^2/\Delta$.

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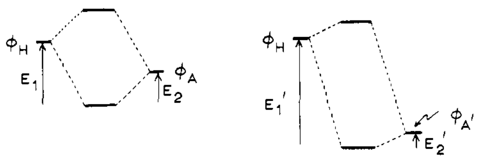

Figure 1. Effect of increasing electron affinity on the energy levels of HA and HA′. The energy of A′ is lower than that of A, and the relative stabilization of the MO is less. The acidity is associated with $2E_2$, the bond dissociation energy with $E_1 + E_2$.

Since the acidity is associated with the transfer of both electrons from ψ to φ_A $(2E_2)$, the energy change, except for the constant Coulombic attraction term, is given by[17]

$$2E_A - 2E_\psi = -\Delta + (\Delta^2 + 4V^2)^{1/2} \qquad (3b)$$

Similarly, the bond dissociation energy corresponds to

$$E_A + E_H - 2E_\psi = +(\Delta^2 + 4V^2)^{1/2} \qquad (3c)$$

Now, as long as the perturbation V remains approximately constant, as may be expected along a row in the periodic table, the energy change for acidity (3b) will decrease as φ_A becomes lower in energy (Δ increases), while the bond dissociation energy (3c) will increase. Thus, as we proceed along a row in the periodic table, given that the electron affinities increase with increasing atomic number, we expect the energy for acid dissociation to decrease and that for bond dissociation to increase.

In considering a column in the periodic table, we note that electron affinities behave somewhat erratically but in any case seem fairly insensitive to atomic number. However, the strength of the perturbative interaction V may now be expected to diminish as we move down the column. This may be a result of a combination of increased electron repulsions as well as changes in overlap. Consequently, if V becomes smaller while Δ remains more or less constant, eq 3b and 3c indicate that both the energy for acid dissociation and that for bond dissociation should decrease as atomic number increases in a given column.

It is clear that all of the trends can be accounted for with this simple picture, although *ab initio* calculations will be necessary to explore the detailed contributions and interactions involved. It is interesting that the solution acidity order of the binary hydrides appears to parallel the gas-phase order. Thus, in the binary hydrides, solvation effects behave in a regular enough way that the intrinsic orders are maintained, in contrast to other series such as alcohols.[2]

A final, curious result of the thermochemical analyses is that ionic dissociation of the type in eq 4 (hydride loss) is more favorable than proton loss for some of the binary hydrides. The EA of H·, 0.76 eV, is high enough that the relative IP's and EA's for systems such as NH_3, PH_3, and H_2S favor this "reverse" dissociation,[18,19] often by a substantial amount. This situation results from the comparatively high ionization potential and modest electron affinity of the hydrogen atom.

$$XH_n \longrightarrow XH_{n-1}^+ + H^- \qquad (4)$$

Experimental Section

All experiments were performed at room temperature on two commercially available (Varian Associates) icr spectrometers. One of these spectrometers, on which intensity *vs.* pressure and intensity *vs.* time studies were carried out, was equipped with an MKS Baratron capacitance manometer with Type 90H-1E head for precise pressure measurement and was also modified by the addition of a trapped-ion analyzer cell.[11]

Gaseous reagents used in these experiments were obtained commercially (Matheson Co.) and were purified by repetitive freeze–pump–thaw cycles. H_2O and n-C_4H_9ONO (used to produce n-$C_4H_9O^-$) were vaporized on a vacuum line and purified by bulb-to-bulb vacuum distillation prior to use. Arsine was prepared by treatment of Zn_3As_2 with HCl followed by vacuum transfer.

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(18) M. J. Woolf, M. Schwarzschild, and W. K. Rose, *Astrophys. J.*, 140, 833 (1964); EA of H·.

(19) Ionization potentials were obtained from J. L. Franklin, *et al.*, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, U. S. Government Printing Office, Washington, D. C., 1969.