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B. E. Mills, R. L. Martin, and D. A. Shirley

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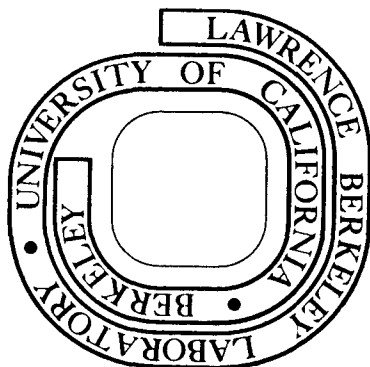
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ABSTRACT: Core-level binding-energy shifts were measured for O1s levels

in alcohols, ethers, acids, aldehydes, esters, and acetone; N1s levels in

ammonia and aliphatic amines, P2p levels in phosphine and its methyl

derivatives, and S2p levels in H_2S and its methyl derivatives. A total of

46 compounds were studied. The core-level shifts correlated well with

gas-phase proton affinities, thereby extending and supporting earlier

results of Martin and Shirley, Davis and Rabalais, and Carroll, Smith, and

Thomas. In the amines, for which the data are most precise, a good corre-

lation was observed for all 16 molecules taken together. On a finer scale,

each series of amines (primary, secondary, tertiary) showed a linear corre-

lation, while ammonia and its methyl derivatives showed a linear correlation

with different slopes. These two correlations are interpreted as responses

of the system to long-range effects and to changes in the local bonds,

respectively. Similar behavior was observed in the single-bonded oxygen

compounds. Excellent linear correlations were observed in the compounds

of the third period elements phosphorus and sulfur. Differences in the

slopes were tentatively attributed to changes in nuclear position on proton-

ation. Analysis of the oxygen data supports the conclusion of Carroll et al

that protonation of carboxyl groups occurs on the keto oxygen. These

results suggest that core level shifts can be used to predict proton affinities.

I. INTRODUCTION

Chemists have devoted considerable effort to understanding the fundamental chemical concept of basicity. In a widely accepted early definition, Brønsted[1] described basicity as the tendency of a molecule B to accept a proton in the reaction

$$B + H^+ \rightarrow BH^+ . \qquad\qquad -PA \qquad\qquad (1)$$

The enthalpy change of this reaction is -PA, where PA is the proton affinity of B. This concept of basicity was generalized further, and freed from reference to a specific acid (H^+) by Lewis, who defined a base as a molecule that tends to donate a valence electron "lone pair" in bonding with a Lewis acid; i.e., a molecule that can accept an electron pair.[2] Thus B in Eq. (1) is also a Lewis base because it contributes a lone pair in forming the $B-H^+$ bond.

Problems are encountered when attempting to relate these concepts to microscopic properties of isolated molecules. Measurements that yield basicity information are hard to make, and few are available. Gas-phase basicities can follow trends opposite to those observed in solution,[3] showing that the solution results may be dominated by solvation effects. It is of considerable importance to be able to separate the local molecular effects from those of solvation, because of the bearing of these two effects on the more general question of solution vs. gas-phase chemical reactivity. Recently Martin and Shirley,[4] and independently Davis and Rabalais,[5] have shown the relationship between trends in basicity and core-level binding energies. They further showed that the trends in general resulted from the interplay of initial-state (inductive) effects and final-state

(polarization) effects, with the latter dominating for the proton affinities and O1s binding energies (E_B(O1s)) of a series of aliphatic alcohols. This can be understood on the basis that the -OH group has essentially the same local charge distribution and electrostatic potential in different alcohols ROH. Introduction of a positive "test charge" — either by adding a proton to form ROH_2^+ or by removing an O1s electron to form a positive 1s hole — is accompanied by a reaction energy that varies with R mainly through the variation of the R group's ability to stabilize the positive charge through polarization. The relation of the O1s binding-energy trends with Lewis basicity is obvious, while its relation with Brønsted basicity is nearly quantitative for the few cores studied in references 4 and 5.

Carroll, Smith, and Thomas[6] added more single- and double-bonded oxygen compounds and some di- and triatomic molecules to the correlation between E_B(O1s) and -PA, and they discussed the position of protonation for some cases. In this paper we report additional O1s and N1s core-level binding energies, and correlations with PA values in series of alcohols, ethers, acids, esters, aldehydes, acetone, and aliphatic amines. The correlation has been extended to the third row by measurements of core-level binding-energy shifts in phosphine and methyl-substituted phosphines, as well as the series H_2S, CH_3SH, $(CH_3)_2S$. Experimental procedures are described in Section II, and results are given in Section III. The results are discussed in the above order in Section IV.

II.   EXPERIMENTAL

All of the compounds were obtained commercially except for $P(CH_3)H_2$, which was made by the method given by Jolly.[7]   The methyl-substituted phosphines were purified on a vacuum line, and their purities checked by vapor pressure measurements.   Gaseous N_2, O_2 and PF_3, which were used as binding-energy standards, were run along with the appropriate compounds. The sulfur compounds were run with Ne as a standard.   The spectra were taken on the 50-cm radius Berkeley magnetic spectrometer using Mg $K\alpha_{1,2}$ radiation.   They were fitted to Gaussian peaks using a non-linear least-squares computer program.   In the case of O_2, the two lines were fixed at an area ratio of 1 to 2 and a separation of 1.12 eV.   For the acids and esters the peaks from the two oxygens were constrained to have the same area.

III.   RESULTS

The binding energy shifts are shown in Table 1 along with the proton affinities for the various molecules studied.   In some cases there was more than one literature value of the PA.   In cases for which there was no clear reason to choose among various proton affinity values, preference was given to data in which an entire series was measured at the same laboratory. The worst disagreement is for acetone, in which the PA values are separated by 14 kcal while the stated errors are 2 kcal.[8,9]

The errors in the relative core binding energies are smaller than the PA errors in the oxygen compounds, amounting to 0.02 - 0.05 eV (0.5 - 1.2 kcal), being largest for molecules containing two oxygens where there is a problem of resolving two close peaks.   This applies to the acids, but

is worse for the esters because of the smaller separation in the ester

peaks. The relative errors in both PA and E_B for the amines are quite

small.

IV. DISCUSSION

The relation of variations in proton affinity (PA), core-binding

energy (E_B), and first (lone-pair) ionization potential (IP) has been

discussed previously.[4] Let us review this relationship briefly from two

different points of view before discussing the data. First, the ionization

potential corresponds to the reaction

$$B: \rightarrow B.^+ + e^- \qquad\qquad IP , \qquad\qquad (2)$$

where, as in Eq. (1), the reaction energy is written on the right.

Combining Eqs. (1) and (2) with the binding energy of atomic hydrogen

$$H \rightarrow H^+ + e^- \qquad\qquad e^2/2a_o , \qquad\qquad (3)$$

we obtain

$$(B:H)^+ \rightarrow B.^+ + H \qquad\qquad HA . \qquad\qquad (4)$$

If the hydrogen affinity HA is constant as the base B is changed, it

follows that $\Delta PA = -\Delta IP$. This condition is surely not satisfied in general,

but we may expect it to be satisfied within a homologous series. For a

series of alcohols ROH, for example, HA should be only weakly dependent

on R. As a first approximation this weak R dependence of HA might be

absorbed as a constant in the ΔPA vs. $-\Delta IP$ relation. Thus PA and -IP would

vary together linearly, though not with unit slope. The core-level binding

energy (E_B) can be incorporated into this linear variation if we note that

E_B and IP should vary together (assuming that the lone pair is really an *atomic* pair), though not with unit slope.[10,11]

The second approach focuses on the similarity among the three processes, which for alcohols can be written

$$R-O\underset{H}{\overset{}{\diagdown}} + H^+ \rightarrow R-O\overset{\diagup H^+}{\underset{H}{\diagdown}} \qquad -PA \qquad (5a)$$

$$R-\ddot{O}\underset{H}{\overset{}{\diagdown}} \rightarrow R-\dot{O}\underset{H}{\overset{}{\diagdown}}{}^+ \qquad IP \qquad (5b)$$

$$R-\overset{}{\Theta}\underset{H}{\overset{}{\diagdown}} \rightarrow R-O\underset{H}{\overset{}{\diagdown}}{}^+ \qquad E_B(O1s) \qquad (5c)$$

These equations were written to emphasize that in each case the ROH molecule is probed by a positive "test charge": the proton, the lone-pair hole, and the 1s hole, at the OH bond distance, the O2p radius, and the O1s radius, respectively. While the absolute magnitudes of PA, IP, and E_B are very different, their *variation* in each case depends largely on the R group's ability to stabilize the added localized positive charge by polarization. Thus as R is varied -IP, PA, and E_B should vary together linearly, though not with exactly unit slope (the slope should be approximately unity[4,5]). Because the "lone pair" can have some molecular orbital character, it is the least reliable test probe. As the R group becomes larger the linear variation should become more reliable, provided that the local environment of the active group is unchanged.

The data are discussed below in groupings that test various aspects of the correlations between E_B and PA.

A.   <u>Singly-Bonded Oxygen</u>

Figure 1 is a plot of E_B(Ols) versus PA for those molecules in which oxygen is only singly bonded. The line of unit slope through the water point falls typically 0.1 eV below the alcohol points and 0.35 eV below the ether points. The latter data sets are each well-fitted by lines of slope 0.95. It appears that substitution of an alkyl group for a hydrogen has a greater effect on E_B(Ols) than on PA, although uncertainties in the PA shifts — which for those compounds are much less accurately known than the E_B(Ols) shifts — leave a small residual doubt about this conclusion. The Ols binding energies for OH groups in acids and esters are not included in Fig. 1 because the proton is believed to attach to the keto oxygen (see below). In fact these OH points would fall more than 1 eV below the lowest line in Fig. 1.

B.   <u>Doubly-Bonded Oxygen</u>

The E_B(Ols) values are plotted against proton affinities in Fig. 2, with the origin at the H_2O point. The acids and esters each showed two equally intense peaks in the Ols spectra, with separations ranging from 1.28 eV to 1.79 eV for the various molecules. It is natural to expect that the lower binding-energy peak belongs to the doubly-bonded oxygen, on chemical grounds, because this oxygen is more negative. As pointed out by Carroll et al.[6], theoretical estimates[12] of the Ols binding energies in formic acid support this assignment. In order to determine which peak corresponds to the carbonyl oxygen without invoking calculations or arguments about charge distribution, a spectrum of

$CH_3O-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3$ (dimethyl carbonate) was obtained. This compound is very

similar in structure to $CH_3(CH_2)-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3$ (methyl propionate) and gives

a similar O1s spectrum except that the high binding energy peak is twice

the area of the other. This must therefore be the ether oxygen, and the

low binding energy peak arises from the carbonyl oxygen. We are therefore

confident that the O1s peaks are correctly assigned in these compounds.

Although the E_B(O1s) data do not by themselves give any indication

of the protonation site in acids and esters, Carroll et al[6] concluded from

the E_B - PA correlation that protonation occurs at the keto oxygen, in

disagreement with the assignment of Pesheck et al.[13] Our results agree

with the assignment of Carroll et al. The "keto" oxygen correlation

coincides with that of the aldehydes and ketones, while the "ether" oxygen

correlation disagrees badly with the alcohol and ether values, as discussed

above. Protonation apparently takes place at the keto oxygen.[14]

The range of E_B(O1s) values in the doubly-bonded oxygen (Fig. 2)

is actually somewhat larger than in the singly-bonded case (Fig. 1). This

occurs in spite of the fact that in the keto linkage the "active" oxygen

atom is always shielded by a carbon atom from shifts arising from changes

of substituents. We believe that the larger range of E_B(1s) values — and

of proton affinities — in the doubly-bonded oxygens arises because of an

additive combination of inductive (initial-state) and polarization (final-

state) effects. In the ether-linkage cases (Fig. 1), by contrast, inductive

shifts were relatively small because varying the alkyl groups did not

change the oxygen charge very much.

The oxygen data can all be fitted reasonably well with the equation

$$PA = PA(H_2O) + 23.05[E_B(O1s,H_2O) - E_B(O1s,X)] - 7 \text{ kcal} \qquad (6)$$

with proton affinities in kcal/mole and binding energies in eV. This

equation should serve to predict proton affinities to ± 5 kcal or better.

Of course it applies only to those oxygens on which proton attachment

occurs.

C.   Nitrogen 1s Binding Energies in Amines

Aliphatic amines comprise another series for which gas-phase PA

values are available. Indeed Aue et al[15] have reported an accurate set

of PA values with small relative errors, although their values for ammonia

and methyl amine were obtained by extrapolation of the PA-IP correlation.

In Fig. 3 we have plotted E_B(N1s) against the PA values. The E_B and PA

scales are both relative, with ammonia taken as the reference compound.

The absolute error in the PA of ammonia is shown in Fig. 3.

In discussing the systematics of the E_B(N1s)-PA correlation, it

is useful to divide the amines into primary, secondary, and tertiary groups,

with methylamine, etc., comprising the first member of each group. We

note first that a straight line of unit slope, Curve A, fits roughly through

all the data. All but four of the sixteen compounds' points fall within

0.1 eV of Curve A, and the worst deviation is 0.15 eV. Thus the relation

$$\Delta E_B = -\Delta PA \qquad (7)$$

is roughly confirmed.

The precision of the amine data permits a more detailed interpre-

tation. Curve B, which is described by

$$\Delta E_B(N1s) = -0.73 \, \Delta PA \qquad (8)$$

passes through ammonia and its three methyl derivatives. Its slope shows

that PA varies faster than E_B(N1s) when methyl is substituted for hydrogen.

Within each amine series (primary, secondary, tertiary), however, the relation

$$\Delta E_B(N1s) \; = \; -1.5 \; \Delta PA \tag{9}$$

fits the data quite accurately. This means that within a series a change of the substituent affects $E_B(N1s)$ more than PA. At first sight this result appears to contradict the IP - PA correlation, in which Aue et al[14] found $\Delta IP \simeq -\Delta PA$ within each amine series.   The homolytic bond dissociation energy HA (see Fig. 4) appeared constant within each series, with a shift from one series to another. In fact we believe that all these observations can be interpreted in a self-consistent way that supports the earlier inter- pretations and yields additional insight into the proton addition reaction.

Two crucial points must be remembered:

1. The IP and PA values are directly sensitive to details of local bonding at the nitrogen site; i.e., changes of angle, hybridization, etc. The $E_B(N1s)$ parameter responds only to a change in the average potential, and may shift less.

2. If the local bonding at the nitrogen atom is kept constant, as in the series of primary amines for example, variations in the alkyl substituents will affect E_B, IP, and PA mainly through electron-electron shielding, either inductively (in the initial state) or through polarization in the final state. In either case the shift in E_B will exceed that in IP or PA.

The first point is consistent with the observation that in the group NH_3, methylamine, dimethylamine, trimethylamine, the three quantities E_B, IP, and PA vary linearly with one another but with slopes very different from unity. The total ranges are $\Delta E_B = -0.7$ eV, $\Delta IP = 2.3$ eV, and

$\Delta PA = -1.0$ eV. The difference in sensitivities of IP on the one hand versus E_B and PA on the other reflects the fact that the latter two quantities measure the molecule's response to a more localized test charge (a 1s hole or a proton), while the IP measure a much more complex property.

The second point can be interpreted more quantitatively. A distant perturbation (such as changing the length of an alkyl group) is felt locally at the nitrogen site through inductive or polarization effects. These are expressed as changes in the electron population in the valence shell of nitrogen in the initial and final states, respectively. In either case the N1s binding energy should vary as the two-electron Coulomb integral $F^O(1s,2p)$ times Δn, the change in valence shell population, while for the IP this integral is replaced by $F^O(2p,2p)$. This leads to larger shifts for inner shells, a well-known effect that has been discussed elsewhere.[10,11] We note that for a proton at the mean radius of the 2p shell in nitrogen the Coulombic interaction with N2p electrons would be of a similar magnitude but opposite sign compared to a 2p electron. We therefore would predict

$$\frac{\Delta E_B(N1s)}{\Delta IP} \cong \frac{F^O(1s,2p)}{F^O(2p,2p)} = 1.45 \quad ,$$

$$\frac{\Delta IP}{\Delta PA} \cong \frac{F^O(2p,2p)}{-F^O(2p,2p)} = -1 \quad ,$$

for the slope within a series of primary, etc., amines. The numerical ratio 1.45 was obtained by using Mann's integrals.[16] The agreement with experiment is excellent (Eq. (9)).

D.   Shifts in Sulfur and Phosphorus

The E_B - PA comparison was extended to third-row elements by

studying H_2S, phosphine, and their methyl derivatives. Sulfur and phos-

phorus differ from oxygen and nitrogen in having larger covalent radii,

low-lying d orbitals, and lower electronegativity. Thus it was not

clear what to expect. Only seven molecules were studied in this first

attempt to extend the E_B - PA correlation to the third row, so only

tentative conclusions can be drawn as yet. Thus far a surprisingly good

correlation appears to exist.

Figure 4 shows a linear E_B(P2p)-PA correlation in the phosphorus

compounds, but the slope is significantly less than one. This is interesting

because the first IP follows the PA much more closely[17] (just the opposite

from the amines). In other words, the homolytic bond dissociation is about

constant. Nuclear rearrangement, or relaxation, in the protonated final

state is important in the phosphines. This nuclear relaxation takes place

upon protonation and with removal of a lone-pair electron (for the *adiabatic*

IP) but not in the case of core ionization. It is possible to estimate

the degree of angular rearrangement of the phosphines from the bond angles

in the corresponding silanes, which are isoelectronic in the valence shells

and have equal core charge. The H-P-H angle in phosphine is 93.3°, and

the protonated ion is tetrahedral (109.5°). The corresponding angle change

in trimethylphosphine is 98.9° to 110.2°. CNDO/2 calculations indicate

that in the ground state the lone pair orbital is mainly s-like, whereas

in the protonated state the P-H bond is more nearly sp^3 in character. The

steric strain moderation on substituting a less repulsive hydrogen for a

lone pair is expected to be greater in the case of the methylated phosphines

than in phosphine itself where the hydrogens are already over 2Å apart

in the initial state. Similar angle opening is expected upon ionization

of one of the lone pair electrons because a single electron is also less

repulsive than a lone pair. Core ionization, however, should not cause

significant angular relaxation. This might account for the poorer

agreement between $-\Delta PA$ and ΔE_B than between $-\Delta PA$ and ΔIP. Of course

there may be another reason for the observed behavior. Perhaps, for

example, the fact that the $\Delta E_B - \Delta PA$ correlation shows a low slope in the

methyl derivatives of nitrogen and phosphorus (-0.7 and -0.6, respectively)

is a clue that the same mechanism is operative in both cases.

In considering the sulfur compounds we first note that there are

only three points and that the PA measurements were done by two different

groups. It may, therefore, be fortuitous that $-\Delta PA = \Delta E_B$ to within

experimental error (Table 1). Unfortunately for geometry change arguments

of the type used above for the phosphines, we do not have the geometries

for CH_3PH_2 or $(CH_3)_2PH$ which are isoelectronic with $CH_3SH_2^+$ and $(CH_3)_2SH^+$.

If we assume, however, that the angles of the above phosphorus compounds

are intermediate between those of PH_3 and $P(CH_3)_3$, the angles between the

ligand bonds in CH_3SH and $C(H_3)_2S$ would *decrease* upon protonation.

Comparison of SH_2 and PH_3 indicates that the H-S-H angle increases by

only 1° upon protonation. While these arguments are not quantitative,

it appears that relief of steric strain in the final protonated state is

less important for the sulfur series.

V. CONCLUSIONS

The binding energy-proton affinity correlation has been extended by this work to forty-six molecules, including molecules containing the third-row elements phosphorus and sulfur. The following conclusions were drawn:

1. The correlation holds up surprisingly well in the main, in both second- and third-row elements.

2. Extension to ethers (from H_2O and alcohols) and to larger alkyl amines shows that two correlations exist. All primary amines fall on one line, for example, while secondary amines are offset. This reflects the relative sensitivities of E_B and PA to long-range inductive effects versus changes in local bonding. It may prove valuable in understanding variations in proton affinity.

3. Further evidence was obtained that protonation of carboxyl groups takes place at the keto oxygen.

4. The small slope of the correlation in phosphine derivatives and the unit slope in H_2S derivatives may be a consequence of nuclear relaxation, because the bond angles appear to change more in the former case.

The main conclusion to be drawn is that these additional results tie core-level binding-energy shifts firmly to a chemical property, the proton affinity. The proton and the core electron can be regarded as two "test charges" that probe both the static (initial-state) and dynamic (final-state) properties of a functional group. Used in a complementary way these two probes may yield insight into the electron dynamics of chemical reactions.

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TABLE 1. Binding energy shift from reference molecule, proton affinity and shifts relative to the basic hydride.

Molecule	$-E_B$ Shift		PA Used	Other PA measurements	$-\Delta E_B$	ΔPA
Water	3.43(2)		165(3)[a]	165(3)[b], 164(4)[c]	0.00	0(3)
Methanol	4.22(2)		180(3)[d]	182(3)[b]	0.79	15(3)
Ethanol	4.53(2)		187(2)[a]	186[d]	1.10	22(2)
Propanol	4.60(2)		189(2)[a]		1.17	24(2)
i-Propanol	4.75(2)		193(5)[a]	193(5)[e], 195[f]	1.32	28(5)
t-Butanol	4.96(2)		198(3)[a]	206[f]	1.53	33(3)
Dimethyl ether	4.74(2)		187(1)[d]	190(5)[a], 186[d], 186[e]	1.31	22(1)
Diethyl ether	5.24(2)		199[b]	205(3)[a]	1.81	34
Formaldehyde	3.77(2)		168(1)[g]	166[d], 165(3)[c]	0.34	3(1)
Acetaldehyde	4.71(2)		185(2)[g]	183(2)[e], 183[d]	1.28	20(2)
Propionaldehyde	4.85(2)		187(2)[g]	187[d]	1.42	22(2)
Acetone	5.37(2)		202(2)[a]	188(2)[b], 196(2)[h], 202[i]	1.94	37(2)
Formic acid	2.65(3)	4.35(3)	175(5)[a]	179(3)[b], 166[j]	0.92	10(5)
Acetic acid	3.20(3)	4.99(3)	188(3)[a]	184(3)[j]	1.56	23(3)
Propionic acid	3.31(3)	5.07(3)	~190[a]	185(3)[j]	1.64	~25
Trifluoroacetic acid	2.00(3)	3.75(3)	167(3)[a]		0.32	2(3)
Methyl formate	3.46(5)	4.86(5)	188(3)[a]		1.43	23(3)
Ethyl formate	3.72(5)	5.01(5)	198(3)[a]		1.58	33(3)
Propyl formate	3.80(5)	5.08(5)	198(3)[a]		1.65	33(3)
Methyl acetate	3.86(5)	5.39(5)	202(2)[a]		1.96	37(2)
Ethyl acetate	4.07(5)	5.49(5)	205(3)[a]		2.06	40(3)
Propyl acetate	4.13(5)	5.55(5)	207(3)[a]		2.12	42(3)
Methyl propionate	4.03(5)	5.58(5)	205(3)[a]		2.15	40(3)
Ammonia	4.41(2)		207(3)[k,l]		0.00	0(3)
Methylamine	4.76(2)		218.4[l]	211(3)[b], 216.3(6)[m]	0.35	11.4
Ethylamine	4.95(2)		221.1(2)[l]	218.8(6)[m]	0.54	14.1(2)
n-Propylamine	5.03(2)		222.3(2)[l]		0.62	15.3(2)
n-Butylamine	5.05(2)		222.8(2)[l]		0.64	15.8(2)
i-Propylamine	5.11(2)		223.3(2)[l]	221.2(6)[m]	0.70	16.3(2)
sec-Butylamine	5.19(2)		224.4(2)[l]		0.78	17.4(2)
t-Butylamine	5.24(2)		225.4(2)[l]	223.3(6)[m]	0.83	18.4(2)
Dimethylamine	5.00(2)		224.9(2)[l]	222.4(6)[m]	0.59	17.9
Diethylamine	5.36(2)		230.1(2)[l]		0.45	23.1
Di-n-propylamine	5.46(2)		231.9(2)[l]		1.05	24.9
Di-n-butylamine	5.50(2)		232.7(2)[l]		1.09	25.7
Di-i-propylamine	5.62(2)		234.3(2)[l]		1.21	27.3

TABLE 1 (continued)

Molecule	$-E_B$ Shift	PA Used	Other PA measurements	$-\Delta E_B$	ΔPA
Trimethylamine	5.11(2)	229.1(2)[l]	226.6(6)[m]	0.70	22.1
Triethylamine	5.59(2)	235.8(2)[l]		1.18	28.8
Tri-n-propylamine	5.71(2)	238.2(2)[l]		1.30	31.2
Phosphine	4.70(2)	187.9[n]		0.00	0.0
Methylphosphine	5.23(2)	206.9[n]		0.53	19.0
Dimethylphosphine	5.55(2)	218.9[n]		0.85	31.0
Trimethylphosphine	5.78(2)	228.0[n]		1.08	40.1
Hydrogen sulfide	0.00	170(3)[k]		0.00	0.0
Methanethiol	0.69(3)	186[d]		0.69(3)	16
Dimethyl sulfide	1.18(3)	197[d]		1.18(3)	27

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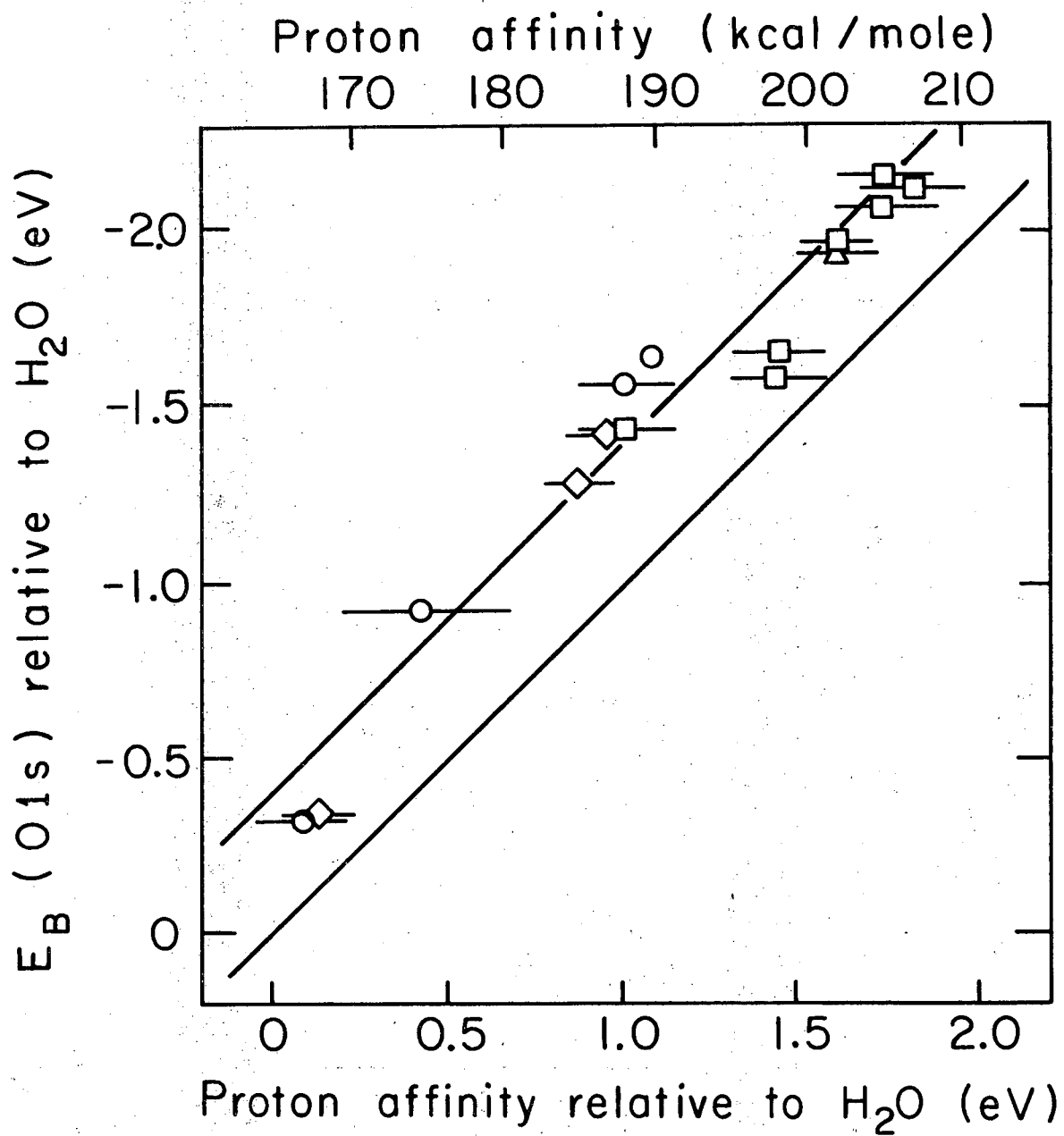[n] R. H. Staley and J. L. Beauchamp, ibid, 96, 6252 (1974).

FIGURE CAPTIONS

Fig. 1. Oxygen 1s binding energies versus proton affinities for single-bonded oxygens. Water is taken as the reference compound. Alcohols are denoted by circles and ethers by squares. The top two lines have slopes of 0.95, and the lowest line has unit slope. Errors in PA are shown: errors in E_B are smaller than symbols.

Fig. 2. Oxygen 1s binding energies versus proton affinities for double-bonded oxygen in acids (circles), esters (squares), aldehydes (diamonds), and acetone (triangle). The two lines of unit slope are offset by 0.4 eV. They pass through the data and the water reference point, respectively.

Fig. 3. Nitrogen 1s binding energies versus proton affinities for a series of aliphatic amines (Table 1), using ammonia (triangle) as a reference. Primary amines are shown as open circles, secondary amines as filled circles, and tertiary amines as squares. Line A has slope unity and is drawn through all the data. Line B connects the ammonia, methylamine, dimethylamine, and trimethylamine points. The other lines show the linear variation within each series.

Fig. 4. Phosphorus 2p binding energy plotted against proton affinity for phosphine and its methyl derivatives. The variation is linear, with a slope of 0.6.
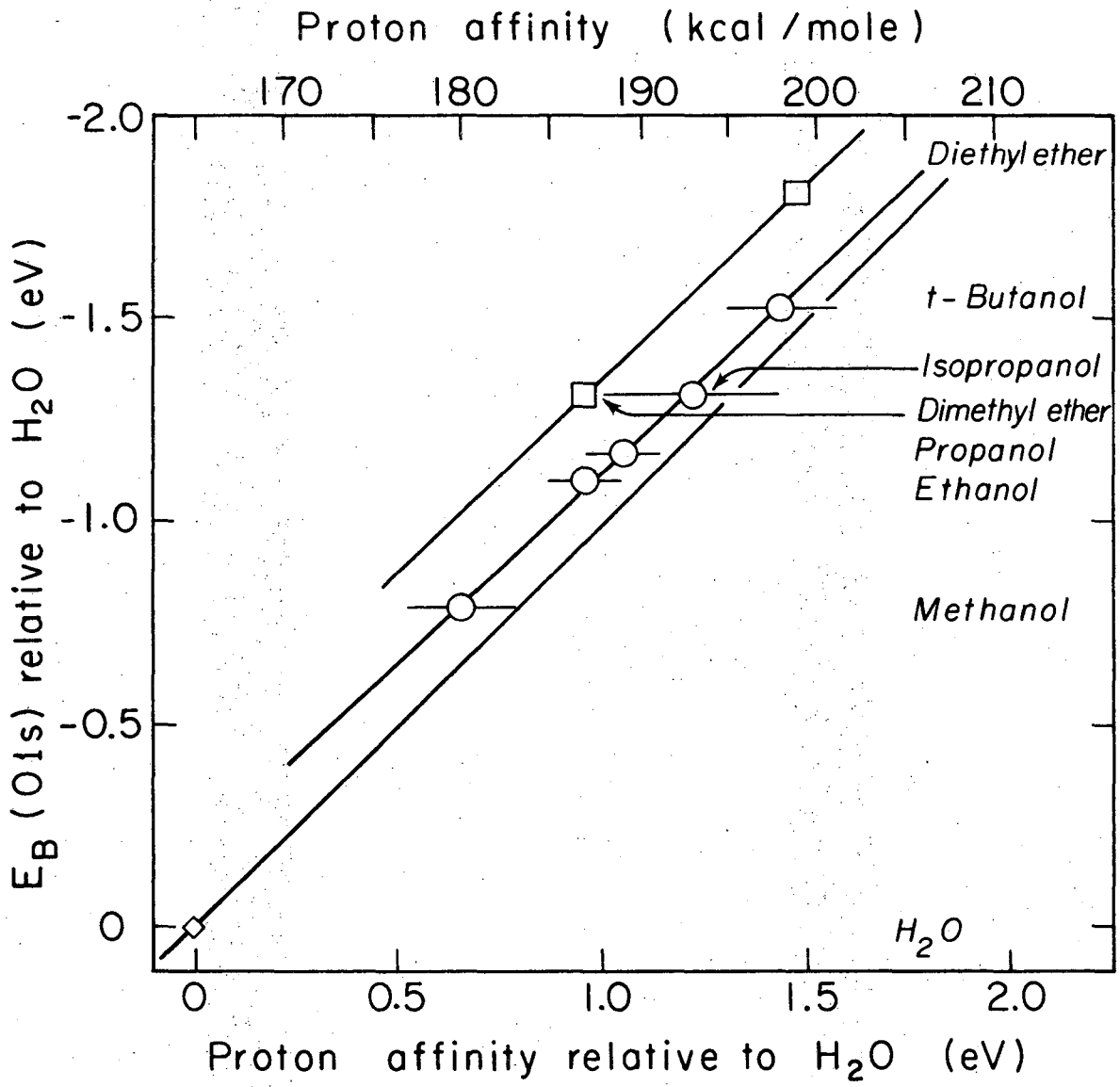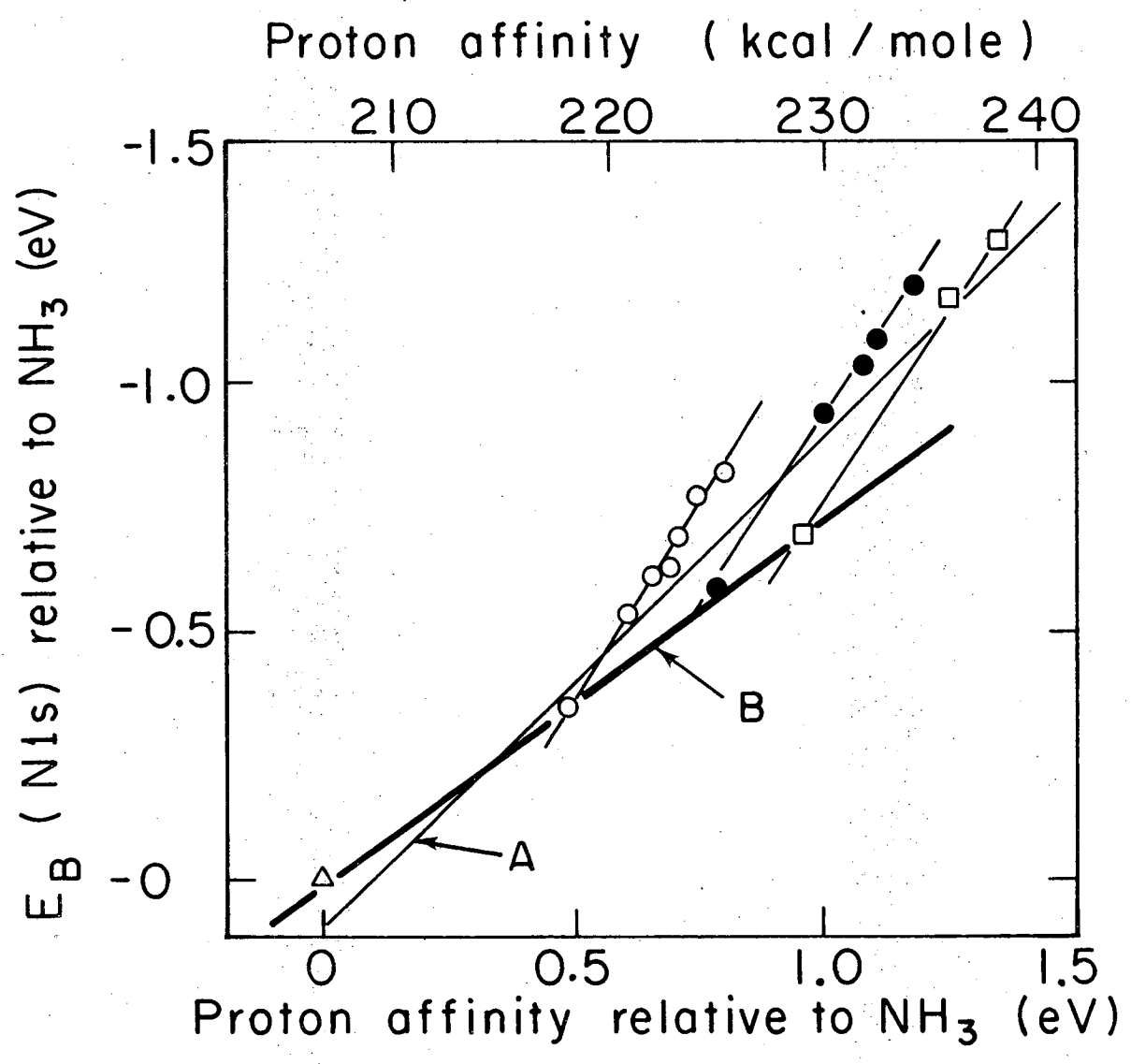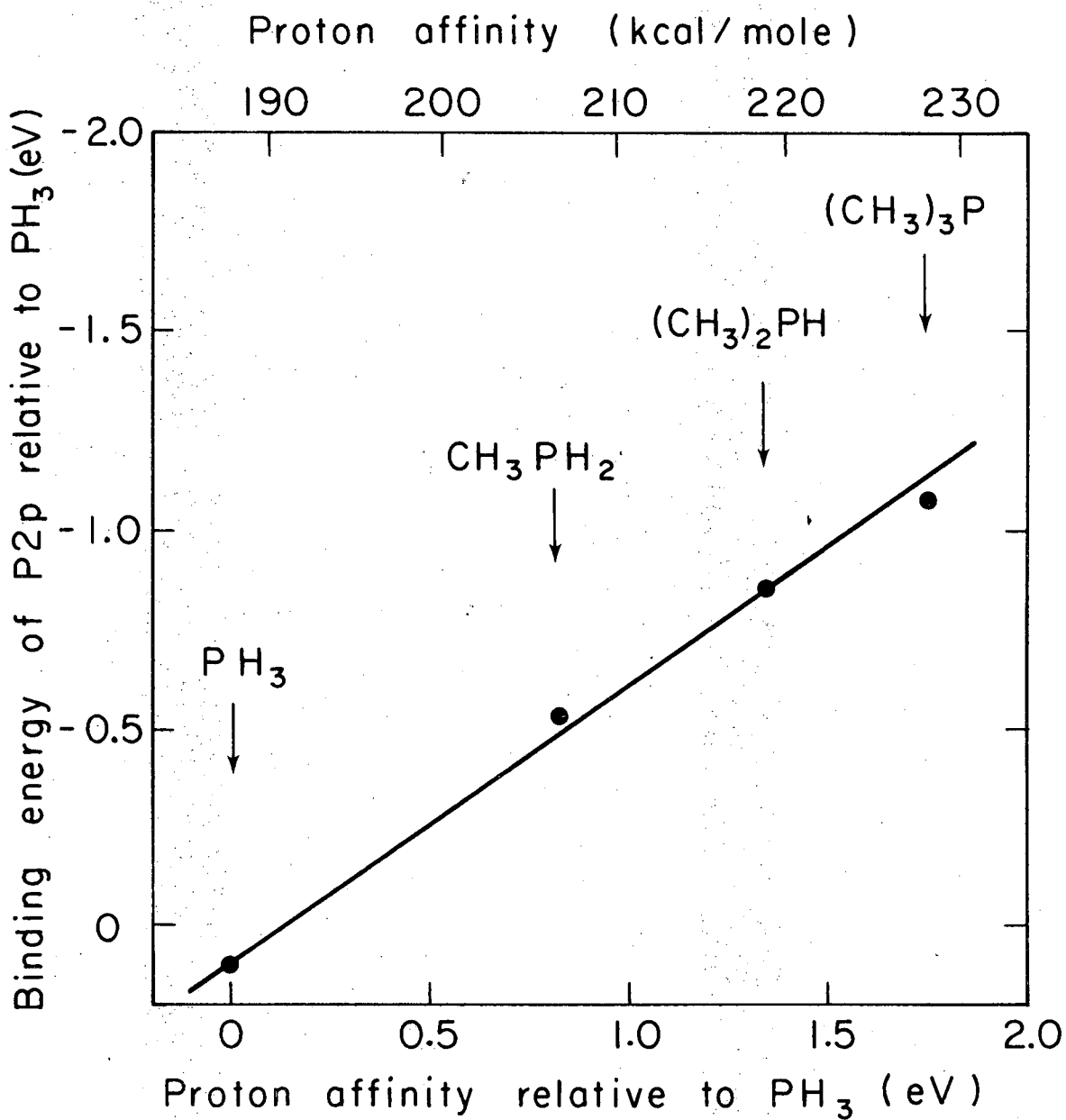
Fig. 1

XBL 756-3296

XBL756 - 3298

Fig. 2

XBL756-3297

Fig. 3

Fig. 4

XBL756-3295