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The Relation of Core-Level Binding Energy Shifts to Proton Affinity and Lewis Basicity¹

R. L. Martin and D. A. Shirley*

Contribution from the Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720.

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Abstract: Gas-phase oxygen 1s binding energy shifts, $\Delta E_B(\text{O } 1s)$, in simple aliphatic alcohols were found to decrease in the order: water > methyl > ethyl > isopropyl > *tert*-butyl. Comparison with potential-model calculations showed that the shifts are attributable to relaxation in the molecular ion final state (polarization effects) rather than to the initial-state charge distribution (inductive effects). The ability of methyl groups to stabilize charge in the ion is consistent with the observation of Brauman and Blair that the gas-phase acidity order is *tert*-butyl > . . . > H₂O. It was predicted that $\Delta E_B(\text{O } 1s) \sim -\Delta(\text{proton affinity})$ for these compounds. In fact the agreement between these two parameters is excellent; thus $\Delta E_B(\text{O } 1s)$ appears to measure relative Brønsted basicities; the $\Delta E_B(\text{O } 1s)$ vs. $-(\text{PA})$ relation may also be applicable to substituted alcohols (the CF₃CH₂OH point agrees very well with the above alcohols) and possibly to other functional groups. The N(1s) binding energy, which decreases in the order NH₃ > CH₃NH₂ > (CH₃)₂NH > (CH₃)₃N, shows excellent agreement with $-(\text{PA})$ in these compounds. The calculated relaxation-energy (or polarization) contribution to ΔE_B for both alcohols and amines agrees very well with the variation in the lone-pair ionization potential, thus giving quantitative support to a suggestion made by Price in 1947. The ΔE_B values for core electrons can be regarded as measuring Lewis basicity if the latter is extended to include nonbonding core orbitals. Thus I(3d_{5/2}) shifts in alkyl iodides are in excellent agreement with the O(1s) shifts in alcohols, with *tert*-butyl iodide being a stronger Lewis base than methyl iodide. Core level shifts may be useful in predicting relative reactivities at different sites in a molecule, because they depend on the proper combination of inductive and polarization shifts. Finally, the inverted acidity order of the aliphatic alcohols in solution may be understood in terms of extramolecular polarization in the final state.

The relationship between molecular structure and reactivity is one of the central problems of chemistry. It may be divided into two parts. *Qualitative* questions about reactivity tend to focus on whether a reaction path exists that can take reactant R to product P. Principles such as orbital symmetry² can be applied to answer these questions. If a path exists for a given type of reaction, we may then be interested in its *quantitative* aspects, e.g., the extent to which the reaction proceeds. An important component of this second part is the relationship between the structures of the reactant and the product and the equilibrium constant for the rapid reversible reaction

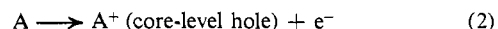


In this paper we shall investigate the way in which a relatively new experimental parameter, the shift in

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

core-level binding energy, can be related to certain reactions of the above type, particularly those involving the gain of a hydrogen ion. In making the analogy between the core-level ionization reaction



and the ionization process



we shall find it useful to generalize further the Lewis concept³ of an acid as an electron acceptor and a base as an electron donor to include core orbitals. By applying principles that have emerged from the theory of core-level shifts, we shall attempt to show how insight can be gained into the relative importance for acid-base reactions of inductive (initial-state) effects and polarization (final-state) effects.

Oxygen 1s binding energies of several simple alcohols were measured in the gas phase to test the ideas de-

(3) G. N. Lewis, "Valence," Dover Publications, New York, N. Y., 1966, p 142.

veloped in this paper. These results are presented in section I. They are compared with proton affinities in section II. The Lewis basicity concept is extended to included core-level binding-energy shifts in section III. Acidities in solution are discussed briefly in section IV.

I. The O(1s) Shifts in Alcohols

Relative core-level binding energies of the oxygen 1s orbital were measured for isopropyl and *tert*-butyl alcohols in the gas phase, using the Berkeley iron-free spectrometer. These were combined with previously reported values for methanol^{4a} and ethanol.^{4b} The experimental techniques have been described earlier.⁵ This series was chosen to determine the effect on the O(1s) binding energy of successive methyl substitution on the adjoining carbon. An internal standard of water was used to enhance the accuracy of the measured shifts. The alcohol O(1s) shifts are given in Table I.

Table I. O(1s) Binding Energy Shifts (eV)

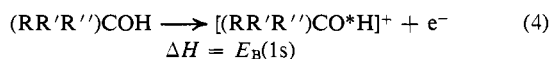
Alcohol	Exptl shift	—Predicted shift ^d —	
		GPM	RPM
H ₂ O	(0.0)	(0.0)	(0.0)
CH ₃ OH	-0.8 ^a	+0.38	-1.08
CH ₃ CH ₂ OH	-1.16 (6) ^b	+0.20	-1.69
(CH ₃) ₂ CHOH	-1.24 (1) ^c	-0.06	-2.26
(CH ₃) ₃ COH	-1.62 (1) ^c	-0.16	-2.59
CF ₃ CH ₂ OH	-0.04 (4) ^b		

^a Reference 3a. ^b Reference 4b. ^c This work. ^d Standard bond lengths and bond angles with the nuclei in staggered rotational conformations were used for the CNDO/2 calculations. See J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

II. Comparison with Proton Affinities

In this section we discuss the relation between core-level binding-energy shifts and basicity. The two subjects are first treated separately, with emphasis on the distinction between inductive and polarization effects.

In photoemission from the oxygen 1s orbital of an alcohol



the O(1s) binding energy $E_{\text{B}}(\text{O } 1\text{s})$ is given by the difference between initial- and final-state energies

$$E_{\text{B}}(\text{O } 1\text{s}) = E_{\text{f}}(\text{RO}^*\text{H}) - E_{\text{i}}(\text{ROH}) \quad (5)$$

An approximate value of $E_{\text{B}}(\text{O } 1\text{s})$ is given by (minus) the O(1s) orbital energy, $-\epsilon(\text{O } 1\text{s})$, which may be obtained directly from a Hartree-Fock calculation on the ground state of ROH. In approximate discussions of core-level binding-energy shifts, it is common to approximate ΔE_{B} by $-\Delta\epsilon$.⁶ Now ϵ and E_{B} are related by

$$E_{\text{B}}^i = -\epsilon^i - E_{\text{R}}^i \quad (6a)$$

$$\Delta E_{\text{B}}^i = -\Delta\epsilon^i - \Delta E_{\text{R}}^i \quad (6b)$$

where E_{R}^i is the "relaxation energy" accompanying loss of an electron from core level i and Δ implies the com-

parison of a given core level (such as O(1s)) between two molecules. The use of $\Delta\epsilon$ for ΔE_{B} is equivalent to considering only the differences between ground-state properties, *i.e.*, inductive effects. This approach is quite useful when inductive effects are dominant. Thus the higher carbon 1s binding energy in CF₄ than in CH₄ is quite properly attributed to the withdrawal of electronic charge from carbon by the four fluorines, leaving a more positive environment at the carbon atom. The C(1s) orbital acts as a probe of the electrostatic potential near the carbon nucleus, and the resultant binding-energy shift can be quite accurately calculated without resorting to *ab initio* SCF methods. Intermediate-level molecular-orbital models such as the CNDO method have been successfully applied to calculate these inductive shifts. For example, a version developed in our laboratory, the ground-state potential model (or GPM) approach, gives good predictions of core-level shifts for certain classes of molecules.⁷ However, the series of alcohols studied in this research does not comprise such a class, and the GPM predictions of O(1s) shifts, listed in Table I, fail to reproduce the experimental trend.

In considering only ground-state, or inductive, effects above we have neglected a crucial parameter of great chemical importance, the internal polarizability of the molecule. As an electron is removed from the O(1s) orbital in an alcohol, other electrons in the molecule are polarized toward the resultant positive hole. Since this polarization occurs adiabatically as part of the photoemission process, it is manifest as a reduction of the binding energy by an amount E_{R} , the "relaxation" energy. Thus ΔE_{B}^i in eq 6b will follow $\Delta\epsilon^i$ only to the extent that ΔE_{R}^i can be neglected. Now it happens that E_{R} has a tendency to increase with molecular size. This can perhaps be best understood if the molecule in its final state is regarded as the neutral molecule plus an electron hole of charge $+e$.⁸ The electronic charge distribution of the molecule will relax to "screen" the hole charge. In effect the hole charge is almost totally screened locally by polarization of charge $\sim -e$ to the oxygen atom. The molecule's excess positive charge thus moves to the outside of the molecule to minimize the Coulombic repulsion. Larger molecules can therefore minimize this repulsion most effectively. Since this process is adiabatic, the polarization occurs without transitions and the final state still has a vacancy in the O(1s) orbital. The dependence of E_{R} on molecular size implies that the alcohols studied here should show a substantial ΔE_{R} effect. From the above argument $E_{\text{R}}(\text{O } 1\text{s})$ should increase from H₂O to *tert*-butyl alcohol, thereby reducing $E_{\text{B}}(\text{O } 1\text{s})$ monotonically from H₂O to *tert*-butyl alcohol, in contrast to the GPM estimates in Table I. Relaxation effects can be taken into account by using another method based on CNDO orbitals, the relaxation potential model (RPM) approach.⁹ RPM values of $\Delta E_{\text{B}}(\text{O } 1\text{s})$, also given in Table I, show much better agreement with experiment than do the GPM estimates. In particular the trend is correctly predicted.

To express the above discussion in chemical terms, the O(1s) photoemission process in eq 4 can be split into two *hypothetical* reactions. In the first an O(1s) electron is removed but the orbitals do not relax and

(4) (a) K. Siegbahn, *et al.*, "ESCA Applied to Free Molecules," North-Holland Publishing Co., Amsterdam, 1969; (b) D. W. Davis, M. S. Banna, and D. A. Shirley, *J. Chem. Phys.*, **60**, 237 (1974).

(5) D. W. Davis, D. A. Shirley, and T. D. Thomas, *J. Amer. Chem. Soc.*, **94**, 6565 (1972).

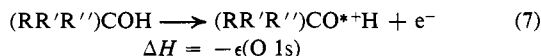
(6) See, for example, D. A. Shirley, *Advan. Chem. Phys.*, **23**, 85 (1973).

(7) D. W. Davis, D. A. Shirley, and T. D. Thomas, *J. Chem. Phys.*, **56**, 671 (1972).

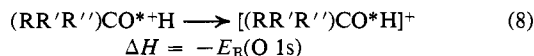
(8) D. A. Shirley, *Chem. Phys. Lett.*, **16**, 220 (1972).

(9) D. W. Davis and D. A. Shirley, *Chem. Phys. Lett.*, **15**, 185 (1972).

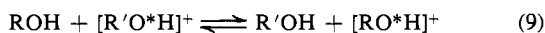
the alcohol goes to an imaginary unrelaxed intermediate state in which the oxygen atom has an additional charge of +1.



Shifts in the energy of this "reaction" are determined by differences in the electron density about the oxygen in the ground state of the alcohol and are *inductive* shifts. In the second step the remaining electronic charge distribution relaxes to screen the positive hole, carrying the molecule into its actual final state.



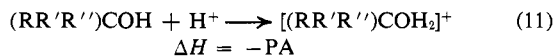
Shifts in the energy of this "reaction" are *polarization* shifts. The two types of shifts are not separately observable because the unrelaxed intermediate state does not really exist. The "reactions" in eq 7 and 8 sum to the real process, in eq 4, for which the energy change $E_B = -\epsilon - E_R$ is observed. Finally, if the O(1s) binding energies between two alcohols ROH and R'OH could be compared at equilibrium



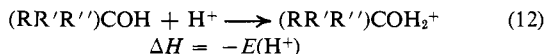
the heat of this reaction would be $\Delta H = \Delta E_B(O\ 1s)$. Neglecting entropy effects the equilibrium constant would be given by

$$K \cong e^{\Delta E_B/kT} \quad (10)$$

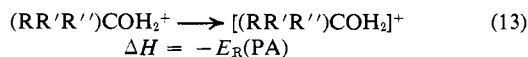
Turning now to the relative basicities of these alcohols, we will argue that the effects which are important in determining the gas-phase proton affinity (PA) of an alcohol are analogous to those which determine the oxygen core-level binding energy. Thus the reaction



is very similar to eq 4. In both cases the alcohol must accommodate to the appearance of a highly localized positive charge on or near the oxygen: an electron hole in the 1s orbital in eq 4 or a proton in eq 11. The proton attachment reactions can also be broken up into two *hypothetical* steps. In the first, the analog of eq 7, the proton would attach to the oxygen without flow of charge in the molecular framework.



Here the product is written to indicate that the excess positive charge is localized on the proton, and $E(H^+)$ would be a "rigid-molecule" proton dissociation energy. In the second hypothetical step the electronic charge in the alcohol relaxes to shield the added positive charge, and the excess charge is effectively distributed over the whole molecule. This step, the analog of eq 8, can be written



where $E_R(PA)$ is a relaxation energy analogous to $E_R(O\ 1s)$ for the photoemission process. For a series of simple alcohols in which the charge on oxygen stays essentially constant from one member of the series to the next, the inductive term, $E(H^+)$ in eq 12, should remain essentially constant. Differences in the induc-

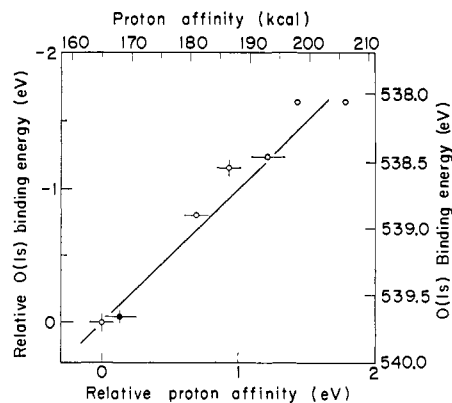


Figure 1. Oxygen 1s binding energies vs. proton affinities for simple alcohols (open circles) and CF_3CH_2OH (filled circle), all in the gas phase. Relative $E_B(1s)$ and PA values are referred to H_2O . The values and references are given in Tables I and II. Compounds in order are: H_2O , CF_3CH_2OH , methanol, ethanol, isopropyl alcohol, and *tert*-butyl alcohol (for which two values of PA are plotted). The straight line has unit slope and goes through the H_2O point.

tive effect throughout the series would be expressed as a variation in the O-H bond strength. As Brauman and Blair have pointed out, however,^{10,11} the O-H bond strength is essentially constant at 104 kcal/mol for all the simple alcohols; thus variations in the proton affinity arise mainly from variations in the "relaxation" term. We then have

$$\Delta(PA) \cong \Delta E_R(PA) \quad (14)$$

For these same alcohols the variations in the O(1s) orbital energy should be small, for the same reasons. Thus from eq 6b

$$\Delta E_B(O\ 1s) \cong -\Delta E_R(O\ 1s) \quad (15)$$

Now eq 8 and 13 are very similar to one another in their overall effect, namely, the relaxation of electronic charge to shield an excess positive charge on or near the oxygen. The incremental relaxation energies ΔE_R should therefore be nearly the same, and from eq 14 and 15 one would expect

$$\Delta(PA) \cong -\Delta E_B(O\ 1s) \quad (16)$$

That is, *the variation in proton affinity of an alcohol should be nearly equal to the variation in the O(1s) binding energy.* The negative sign in eq 16 is a consequence of the sign conventions for binding energy and proton affinity.

That eq 16 is rather accurately obeyed by the simple alcohols is illustrated in Figure 1, in which the binding energy shifts for the simple alcohols from Table I are plotted against the proton affinities of these alcohols,¹²⁻¹⁴ listed in Table II. Also plotted is the CF_3CH_2OH point, to be discussed below. The good agreement between these two quantities provides a striking illustration of the close connection between core-level binding-energy shifts and chemical properties. We

(10) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **90**, 6561 (1968).

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

(12) J. L. Beauchamp and M. C. Caserio, *J. Amer. Chem. Soc.*, **94**, 2638 (1972).

(13) J. Long and B. Munson, *J. Amer. Chem. Soc.*, **95**, 2427 (1973).

(14) D. H. Aue, University of California at Santa Barbara, private communication.

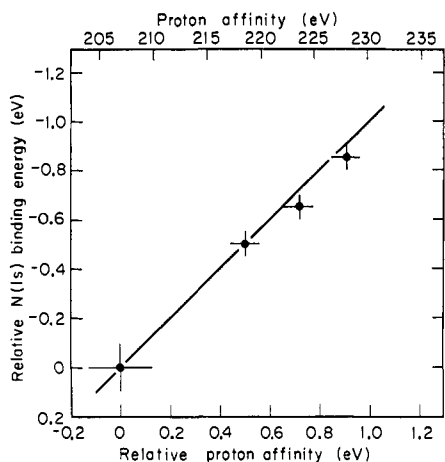


Figure 2. Nitrogen 1s binding energies vs. proton affinities for (from left) NH_3 , methylamine, dimethylamine, and trimethylamine. The PA values plotted are the average of those given in ref 16 and 17. The error on the NH_3 point is absolute, while the others are relative. The straight line through the NH_3 point has unit slope.

Table II. Proton Affinities in Simple Alcohols (kcal)

Compd	PA	Compd	PA
H_2O	165 (2) ^a	Ethanol	186 (2) ^a
$\text{CF}_3\text{CH}_2\text{OH}$	168 (3) ^b	Isopropyl alcohol	193 (3) ^a
Methanol	181 (2) ^a	<i>tert</i> -Butyl alcohol	198, 206 ^a

^a These proton affinities are adopted values, from ref 12–14, with the estimated error in the last digit given parenthetically. Two values have been given for *tert*-butyl alcohol; both are listed.

^b J. L. Beauchamp, private communication.

note that this is not just an empirical correlation of unknown origin but a straightforward consequence of a molecule's electronic charge distribution relaxing to shield an excess positive charge in two similar processes.

Before seeking to generalize the above results we must issue a *caveat*. The confirmation of eq 16 in Figure 1 does not guarantee that the above argument is completely correct. In particular it does not imply that the quantities plotted are almost entirely variations in relaxation energies, as eq 14 and 15 would imply. In fact both the theoretical results in Table I and further evidence to be presented below imply that $\Delta(\text{PA})$ and $\Delta E_{\text{B}}(\text{O } 1\text{s})$ do in large measure arise from their ΔE_{R} terms. For this comparison of $\Delta(\text{PA})$ with $\Delta E_{\text{B}}(\text{O } 1\text{s})$, however, inductive (initial-state) effects would also make these two parameters tend to vary together. This is readily illustrated by rewriting eq 6b for this case and its proton-affinity analog derived from eq 11 and 12.

$$\Delta E_{\text{B}}(\text{O } 1\text{s}) = -\Delta\epsilon(\text{O } 1\text{s}) - \Delta E_{\text{R}}(\text{O } 1\text{s}) \quad (6\text{b}')$$

$$-\Delta(\text{PA}) = -\Delta E(\text{H}^+) - \Delta E_{\text{R}}(\text{PA}) \quad (17)$$

If, in going from one alcohol to another, the oxygen becomes more negative, for example, then $\epsilon(1\text{s})$, which is always negative for bound states, will increase, thereby decreasing $E_{\text{B}}(\text{O } 1\text{s})$. The "rigid molecule" (inductive) contribution to the proton affinity, $E(\text{H}^+)$, will of course increase, as will PA, and $-\Delta(\text{PA})$ will also be negative. Thus inductive effects as well as relaxation effects would shift $-\Delta(\text{PA})$ and ΔE_{B} similarly, and eq 16 would still tend to hold.

From the above reasoning we can make, as a first step toward generalizing, the rather tentative suggestion that proton affinities and core-level binding-energy shifts may be comparable among a wider range of compounds than just the essentially nonpolar simple alcohols. The comparison can be extended in two steps. First, a wider variety of functional groups could be considered. Thus methoxy, phenyl, or CF_3 groups could be attached to the α carbon, for example, and the resulting O(1s) binding-energy shifts could be compared with known proton affinities, to test the prediction that $\Delta E_{\text{B}}(\text{O } 1\text{s}) = -\Delta(\text{PA})$. Data on only one compound appear to be available for testing this prediction: the proton affinity and O(1s) binding-energy shift in $\text{CF}_3\text{-CH}_2\text{OH}$. When plotted on Figure 1, the $\text{CF}_3\text{CH}_2\text{OH}$ point shows excellent agreement with the trend for the simple aliphatic alcohols. We note that substitution of CF_3 for CH_3 in ethanol shifts both its PA and $E_{\text{B}}(\text{O } 1\text{s})$ by about 1 eV. More data will be required before a definitive comparison can be made.

A second, larger extension would include other oxygen-containing functional groups in the comparison. Thus the proton affinities and O(1s) binding-energy shifts in alcohols and acids could be compared, for example, to test the predicted $\Delta E_{\text{B}}(\text{O } 1\text{s}) = -\Delta(\text{PA})$ relation. Unfortunately, there are not enough O(1s) binding energies and proton affinities available for the same molecules to test the validity of either of these extensions. It seems probable that the first prediction should hold, but the second is less likely to, because molecular geometries of different functional groups can change on proton attachment, while there is no geometry change on X-ray photoemission.

A somewhat different case is readily tested. This is the relation between the nitrogen 1s binding energy shifts, $\Delta E_{\text{B}}(\text{N } 1\text{s})$,¹⁵ and the variation in proton affinities^{16,17} of the series NH_3 , CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$, and $(\text{CH}_3)_3\text{N}$. Very good agreement between these two quantities is found, as indicated in Figure 2. This agreement is particularly impressive because in this case methyl groups are directly substituted for hydrogens on the photoemitting nitrogen atom. The reason that the range of $\Delta E_{\text{B}}(\text{N } 1\text{s})$ and $\Delta(\text{PA})$ is only about 1 eV for these amines appears to be that the inductive and polarization effects oppose one another, with the trend determined by the dominant polarization effect. Thus $E_{\text{B}}(\text{N } 1\text{s})$ is larger in NH_3 than in $(\text{CH}_3)_3\text{N}$ even though the methyl groups tend more to withdraw electronic charge from N than do the hydrogens.⁴ We infer from this result and the agreement between $\Delta E_{\text{B}}(\text{N } 1\text{s})$ and $-\Delta(\text{PA})$ that the *sign* of the variation in the gas-phase proton affinity for these amines is attributable to final state polarization effects.

Another outgrowth of the above analysis is a possible explanation of the variation of the first ionization potential within these series of alcohols and amines. The first ionization potential decreases with methyl substitution in each case, by 2.64 eV from H_2O to *tert*-butyl alcohol¹⁸ and by 2.33 eV from NH_3 to $(\text{CH}_3)_3\text{N}$.¹⁶

(15) P. Finn, R. K. Pearson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, **10**, 378 (1971).

(16) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Amer. Chem. Soc.*, **94**, 4726 (1972).

(17) W. G. Henderson, M. Taagepera, D. Holtz, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 4728 (1972).

(18) A. D. Baker, D. Betteridge, N. R. Kemp, and R. E. Kirby, *Anal. Chem.*, **43**, 375 (1971).

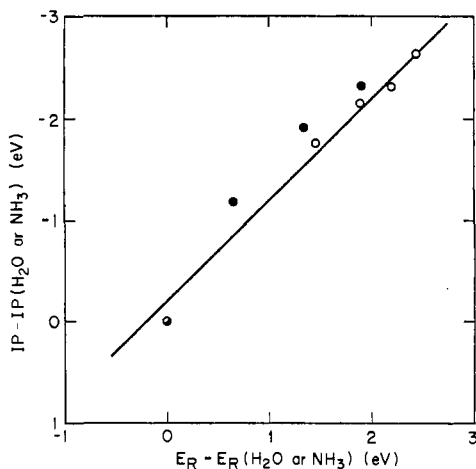


Figure 3. Differences in lone-pair ionization potentials *vs.* differences in calculated relaxation energies for amines (filled circles, from left, NH_3 , methylamine, dimethylamine, trimethylamine) and alcohols (open circles, from left, H_2O , methyl, ethyl, isopropyl, *tert*-butyl alcohol). The straight line has unit slope.

Many attempts have been made over the years to explain these variations in terms of chemical properties, particularly inductive effects due to methyl substitution. However, Price suggested as early as 1947 that “charge-transfer effects” in the molecular ion could account for a relatively large stabilization in the ion and a consequent lowering of the first ionization potential accompanying alkyl substitution.¹⁹ Inasmuch as the first ionization potential can be associated with ionization of an electron from the relatively localized nitrogen or oxygen lone-pair orbital in these compounds, we may identify the above “charge-transfer effects” as flow of electronic charge toward the N or O atom during photoemission. The relative stabilization energy would therefore be given approximately by the relative relaxation energy, which has been calculated for the alcohol (Table I, using $\Delta E_R = \Delta E_B(\text{GPM}) - \Delta E_B(\text{RPM})$) and the amines (Table III of ref 4, using $\Delta E_R = \Delta V_R$). The variation in ionization potential would then be given by

$$\Delta(\text{IP}) \cong -\Delta E_R \quad (18)$$

This relationship actually holds surprisingly well, as shown in Figure 3, especially for the carbon-containing molecules in each group. This good agreement appears to establish the polarization (or extraatomic relaxation) effect as the main contributor to the variation in the first ionization potential in these alcohols and amines.

III. An Extension of Lewis Basicity

Lewis generalized the concept of basicity by defining a base as a substance having a lone pair of electrons that could be used to complete the valence shell of another atom.³ This freed discussions of basicity from the necessity of including any particular ion, such as H^+ . From the preceding discussion of proton affinities and electron-binding energies, it is evident that, while the former measure the Brønsted basicity, the latter are closely related to the Lewis basicity. In fact we need only extend Lewis's definition of basicity to include core-level “lone-pairs” as well as those in the valence shell in order to utilize core-level binding-energy

(19) W. C. Price, *Chem. Rev.*, **41**, 257 (1947).

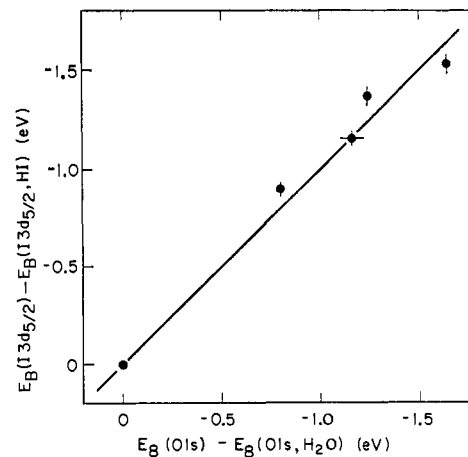


Figure 4. Oxygen 1s binding energies in simple alcohols ROH *vs.* iodine $3d_{5/2}$ binding energies in corresponding alkyl iodides RI (from left R = H, methyl, ethyl, isopropyl, *tert*-butyl). The (HI, H_2O) point is taken as a reference and only relative errors on other points are shown. The straight line through the reference point has a slope of unity.

shifts as one operational measure of the Lewis basicity. We do not intend to imply that the core level participates in the bonding; we are merely noting that these shifts, and the basicity, are comprised of two parts: the initial-state inductive effects and the final-state polarization effects. In studying chemical reactivity we are interested in both effects, in the particular combination given by the binding-energy shifts, rather than just the initial-state charge distributions. This combination of effects would be expected to carry over from the Brønsted bases discussed in section II to compounds exhibiting Lewis basicity as defined above. Two examples of cases for which this result appears to be established are discussed below.

Iodine $3d_{5/2}$ core-level shifts and 5p lone-pair shifts in HI and various iodides were reported and compared earlier.²⁰ The shifts were interpreted at that time as arising from inductive effects. It seems probable, however, in light of the foregoing discussion, that final-state polarization is in fact the dominant factor in these $\text{I}(3d_{5/2})$ shifts. If this is the case, one would expect the $\text{I}(3d_{5/2})$ binding energies to decrease in the order $\text{HI} > \text{methyl} > \text{ethyl} > \text{isopropyl} > \text{tert-butyl}$ and to vary as do the $\text{O}(1s)$ shifts in the corresponding alcohols. Figure 4 shows that these expectations are quite accurately borne out.

Another case in which final-state polarization appears to be important is that of substituted nitroxides. The average $\text{N}(1s)$ binding energy is 410.4 eV in NO, but it drops to 406.8 eV in di-*tert*-butyl nitroxide.²¹ Since the two *tert*-butyl groups do not appear to contribute much electron density to the nitroxide group in the initial state, it appears that this 3.6-eV shift arises mainly through polarization in the final state. Indeed, electron population calculations based on the RPM model bear this out.²²

In both of these cases core-level binding-energy shifts have been associated with Lewis basicity. Thus, for example, *tert*-butyl iodide appears to be a much stronger

(20) J. A. Hashmall, B. E. Mills, D. A. Shirley, and A. Streitwieser, Jr., *J. Amer. Chem. Soc.*, **94**, 4445 (1972).

(21) D. W. Davis, R. L. Martin, M. S. Banna, and D. A. Shirley, *J. Chem. Phys.*, **59**, 4235 (1973).

(22) Reference 21, Table III.

base than methyl iodide. This difference appears to arise not through any significant difference in the ionicity of the C-I bonds in the two molecules but rather because the *tert*-butyl group can more readily accommodate to the loss of an electron, by final-state polarization. While a given *tert*-butyl compound is a stronger Lewis base than is its methyl analogue (e.g., *tert*-butyl alcohol > methanol by 0.82 eV, *tert*-butyl iodide > methyl iodide by 0.63 eV), because of a greater ability to stabilize excess positive charge, *tert*-butyl compounds are also better Brønsted acids because of their greater ability to stabilize excess negative charge, as indicated by Brauman and Blair.¹¹ Final-state polarization also appears to account for the greater speed of substitution of *tert*-butyl alcohol by nucleophilic groups.²¹ In this case the charged "final state" is in fact the transition state of the reaction. The charged carbonium ion is stabilized by polarization in the *tert*-butyl case, thereby lowering the activation energy. We note finally that internal core-level binding-energy shifts among atoms of a given element at different sites in a particular molecule would allow the determination of the relative Lewis basicities of these sites, thereby leading to the possibility of predicting which are the reactive sites in the molecule.

IV. On Relative Acidities in Solution

From the above comparison of gas-phase proton affinities and core-level and lone-pair binding-energy shifts, it seems very probable that the relative gas-phase acidities of the simple alcohols should vary in the order *tert*-butyl > isopropyl > ethyl > methyl > water. In fact this order was established experimentally by Brauman and Blair.^{10,11} These workers suggested that this gas-phase acidity order arises through internal polarization of the alkyl groups in the ion by the localized charge on the oxygen. In essence this is exactly what

we are suggesting to explain the observed values ΔE_B (O 1s) and $\Delta(\text{PA})$ in these alcohols.

Returning to aqueous solutions, Brauman and Blair attributed the reversal of acidity order to steric hindrance of solvation in the larger alkoxides. They further referred briefly to intramolecular polarizability as a kind of internal solvation,¹¹ which they noted would be smaller than the free energy of solvation in a protic solvent, thus accounting for the reversal of acidity order in water.

We fully concur with this explanation of the acidity reversal. However, since we have approached the problem from a different direction, that of understanding gas-phase core-level binding-energy shifts, we find it useful to describe this phenomenon somewhat differently. The O(1s) core-level binding energy in the gas phase decreases with increasing molecular size from H₂O to *tert*-butyl alcohol largely because of extratomic relaxation (final-state polarization). Extramolecular relaxation, or polarization of the surrounding medium, is also possible if the same molecules are studied in solution. This effect would be greatest for the ionization of H₂O and least for *tert*-butyl alcohol, because the bulky *tert*-butyl group will keep solvent molecules away from at least one side of the -OH group. In going from the gas phase to any solution the O(1s) binding energy of *tert*-butyl alcohol should therefore be increased relative to that of water, and the relative acidity of *tert*-butyl alcohol should be reduced. Thus, whereas Brauman and Blair referred to the final-state polarization as an internal solvation, it is also perhaps useful to consider solvation as augmenting the final-state polarization through polarization of the medium.

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