Why Are Organic Acids Stronger Acids than Organic Alcohols?

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Abstract: Comparison of experimental gas-phase acidities and oxygen core-ionization energies of acetic acid and phenol with those of aliphatic alcohols provides insight into the reasons for the acidity of acetic acid and phenol. Contrary to the generally accepted view, resonance delocalization of negative charge in the anion plays only a minor role in determining the relative acidity of these compounds. The higher acidity of the acids arises principally because the electrostatic potential at the acidic hydrogen is more positive in the neutral acid molecule than in a similar alcohol. Quantum mechanical calculations of the initial-state potential and final-state relaxation in phenol, acetic acid, cyclohexanol, and 2-propanol support this view.

As is well known, carboxylic acids and aromatic alcohols are more acidic than aliphatic alcohols. The usual explanation[1] for this difference is that resonance stabilization is greater for acidic anions than for the un-ionized acids. This leads to a lower energy of ionization for the acids than for aliphatic alcohols, where no resonance stabilization is possible for either the anion or the neutral molecule. In this description, the important factor is the electronic rearrangement that takes place after proton removal. This is thought to be greater (and hence, more stabilizing) for acidic anions than for anions derived from alcohols.

We present here both experimental and theoretical evidence that the difference in final-state relaxation between the two types of anion is, in fact, small and has only a minor effect on the relative acidities. We find that the major difference between alcohols and acids is in the charge distribution of the neutral molecule, which establishes a potential at the hydroxyl proton that is more positive (and, hence, less attractive) in acids than in alcohols.

Basic Considerations

Many chemical phenomena depend on the ability of a molecule to accept charge at a particular site. Among these are acidity, basicity, ionization energy, hydrogen bonding, and rates of acid- and base-catalyzed reactions. It is useful to divide the energy for such processes into two parts: an initial-state (potential) energy, which is due to the charge distribution in the original molecule, and a final-state (relaxation) energy, which arises from the rearrangement of valence electrons in response to the newly added charge.

At first glance, this division may appear to be artificial, since it is not obvious how one would sort out the contributions of the two effects: initial-state charge distribution and final-state charge rearrangement. However, the energies involved in these two phenomena can be given a clear theoretical definition and can be experimentally measured by the comparison of core-ionization energies with either gas-phase acidities or Auger energies. A simple classical argument, outlined in the following paragraphs, illustrates the underlying physical principles. These ideas have been developed more fully and quantum mechanically elsewhere.[2-6]

A quantum mechanical derivation of the relationship between acidity and initial- and final-state properties is given in the Appendix of this paper.

In the classical model, the molecule is treated as a polarizable medium containing an atom of charge qe. To this atom is added one unit of charge (positive or negative), giving a new localized charge of $(q \pm 1)e$. Before the charge is changed, the atom is subject to some electric potential, Φ_q, which arises from the distribution of charges in the surrounding medium. We can write

$$\Phi_q = \Phi_0 - \alpha' qe \qquad (1)$$

In this expression Φ_0 represents the potential due to the charge distribution that would exist if $q = 0$, and there is, therefore, no polarization of the surroundings. The second term shows the change in potential due to the polarization of the medium by the charge q; the constant α' is closely related to the polarizability of the surroundings. The minus sign reflects the fact that a positive charge will induce a local negative field and a negative charge will induce a local positive field.

As additional charge edq is introduced at the site of interest there will be a change in energy

$$dE = \Phi_q edq \qquad (2)$$

Integrating from q to $q + 1$ gives ΔE_+, the energy needed to remove an electron.

$$\begin{aligned} \Delta E_+ &= \Phi_0 e - \alpha' qe^2 - \alpha' e^2/2 \\ &= \Phi_q e - \alpha' e^2/2 \\ &= V_q - \alpha/2 \end{aligned} \qquad (3)$$

In the last line of eq 3, we have set $\Phi_q e$ equal to V_q and have replaced $\alpha' e^2$ with α. By similar arguments, ΔE_-, the energy to remove a proton, is given by

$$\Delta E_- = -V_q - \alpha/2 \qquad (4)$$

(Note that the quantity V_q appearing in eq 3 and 4 has a different value in these two different situations. Since the original molecule is neutral the potential at a bound electron must be positive and that at a bound proton must be negative. Thus ΔE is positive in both cases. We will, however, only be concerned with *changes*

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Table I. Potentials (Volts), Potential Energies (eV), and Relaxation Energies (eV)[a]

molecule	method	$\Phi(O)$	$\Phi(O^*)$	$\Phi(H)$	$\Phi(H^*)$	$\Delta V(O)$	$\Delta R(O)$	$\Delta V(H)$	$\Delta R(H)$
C_6H_5OH	G-82(3-21G)	-603.21	-706.51	-25.83	-9.16	1.35	0.09	1.20	0.21
$C_6H_{11}OH$	G-82(3-21G)	-604.56	-707.69	-27.03	-10.78	0	0	0	0
C_6H_5OH	CNDO	-189.43	-237.52	-25.68	-9.20	1.17	0.51	0.94	0.43
$C_6H_{11}OH$	CNDO	-190.60	-237.67	-26.62	-11.00	0	0	0	0
CH_3COOH	G-82(3-21+G)	-601.37	-704.68	-24.63	-9.18	1.93	-0.15	1.72	-0.46
$(CH_3)_2CHOH$	G-82(3-21+G)	-603.30	-706.91	-26.35	-9.98	0	0	0	0
CH_3COOH	G-82(3-21G)	-602.56	-705.27	-25.37	-10.05	1.91	-0.14	1.62	-0.38
$(CH_3)_2CHOH$	G-82(3-21G)	-604.47	-707.46	-27.00	-10.91	0	0	0	0
CH_3COOH	CNDO	-189.49	-235.80	-25.78	-10.83	1.11	-0.25	0.75	-0.16
$(CH_3)_2CHOH$	CNDO	-190.59	-237.41	-26.52	-11.26	0	0	0	0

[a] $\Phi(O)$ = potential at the acidic oxygen. CNDO does not include contribution from O 1s electrons. $\Phi(O^*)$ = potential at the hydroxyl oxygen for a molecule in which the oxygen is core ionized, calculated by using the equivalent-cores approximation, in which the oxygen atom is replaced by a fluorine atom and the basis functions for oxygen are replaced by those appropriate for fluorine. CNDO does not include contribution from O 1s electrons. $\Phi(H)$ = potential at the acidic proton. $\Phi(H^*)$ = potential at the site of the acidic proton in the neutral molecule, calculated for the anion. $\Delta R(O)$ = relaxation energy calculated by using eq 6. $\Delta R(H)$ = relaxation energy calculated by using eq 7.

in V_q as substituents on the molecule are changed. These will affect the two values of V_q in the same way and the two values of ΔE according to the sign in front of V_q.)

In eq 3 and 4, V_q represents the effect of the initial charge distribution and can be readily determined theoretically from an electronic structure calculation for the molecule. The term $\alpha/2$ is the contribution to ΔE from rearrangement of valence electrons after the electron or proton is removed. It can be evaluated by noting that after the removal of an electron the new potential, Φ_{q+1}, is given by

$$\Phi_{q+1} = \Phi_0 - \alpha'(q + 1)e = \Phi_q - \alpha'e \qquad (5a)$$

Multiplying eq 5a by e gives

$$V_{q+1} = V_q - \alpha \qquad (5b)$$

which upon rearrangement gives

$$\alpha = V_q - V_{q+1} \qquad (6)$$

Alterntively, α can also be evaluated in a similar manner by considering proton removal giving

$$\alpha = V_{q-1} - V_q \qquad (7)$$

V_{q+1} and V_{q-1} can be readily evaluated from electronic structure calculations for the final states after electron or proton removal. This procedure, suggested by Hedin and Johansson,[7] leads to the relaxation potential model used by Davis and Shirley for the calculation of shifts in core-ionization energies[3] and relative gas-phase acidities.[4] Thus both the initial-state and final-state contributions to ΔE are well-defined and easily evaluated.

From an experimental point of view, we note that ΔE_+ is the ionization energy, I, for an electron, provided that the model is limited to core electrons, which are well localized. We are concerned with shifts in core-ionization energies, ΔI, for similar electrons in different environments (for example, the difference between the oxygen 1s ionization energy in phenol and cyclohexanol). Replacing the quantity $\alpha/2$ in eq 3 with R (for relaxation energy) and dropping the subscript q, we have

$$\Delta I = \Delta V - \Delta R \qquad (8)$$

Similarly, ΔE_- is the energy to remove a proton, or the gas-phase acidity, A. Comparing acidity in different molecules, we have

$$\Delta A = -\Delta V - \Delta R \qquad (9)$$

(A quantum-mechanical derivation of eq 7 and 9 is given in the Appendix.) From eq 8 and 9 and the appropriate experimental results, the contributions of the initial-state potential and final-state charge rearrangement can be readily determined.

$$\Delta R = (-\Delta I - \Delta A)/2 \qquad (10)$$

$$\Delta V = (\Delta I - \Delta A)/2 \qquad (11)$$

This method has been used by Smith and Thomas[8] to determine

experimental values of ΔV and ΔR in a variety of substituted carboxylic acids. Their results are in good agreement with the-oretical values calculated as outlined above by Davis and Shirley.[4]

Theoretical Calculations

We have used both an ab initio method (Gaussian 82: restricted Hartree–Fock type calculation with the 3-21G basis set) and the CNDO/2 method to calculate charge distributions in acetic acid, 2-propanol, phenol, cyclohexanol, the anions obtained by removing the acidic proton from these molecules and the core-ionized ions obtained by removing a 1s electron from the hydroxyl oxygen. Since the 3-21G basis set does not give an accurate description of the electronic structue of anions,[9] we have also done calculations for acetic acid, 2-propanol, and their anions using the 3-21+G basis set. The parameters for the diffuse orbitals used in these calculations are those suggested by Clark et al.[9] Although the results of the calculations with different basis sets differ in detail, the conclusions about the relative importance of initial- and fi-nal-state effects are independent of the choice of basis set or even the choice of ab initio or semiempirical theory.

For acetic acid[10] and phenol[11] we have used bond lengths and bond angles from electron diffraction and microwave measure-ments. For 2-propanol[12] and cyclohexanol[13] we have used standard lengths and angles. In each case, the geometry of the anion was taken to be the same as that for the neutral species. Calculations with other geometries for the neutral species or for geometrically relaxed anions showed that our conclusions do not depend critically on the geometry.[14]

From the calculated results we have determined the initial-state and final-state potentials, Φ_q and Φ_{q-1}, respectively, at the location of the acidic hydrogen. These potentials are readily evaluated from the wave functions given by the ab initio calculations. For the CNDO results we have assumed a point-charge model for the Coulomb interaction between the hydrogen and the other atoms and that the potential energy due to an electron localized on the hydrogen is $(q_H - 1)$ atomic units, where q_H is the atomic charge on the hydrogen. We have also calculated the potential at the

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(12) Calculations of 2-propanol, its anion, and the core-ionized species were obtained by using the following structural parameters: C–C = 1.54 Å, C–O = 1.45 Å, C–H = 1.09 Å, O–H = 0.958 Å with bond angles of 109.5 ± 0.5°. The hydrogen attached to carbon number 2 was fixed in the anti conformation with respect to the hydroxyl hydrogen.
(13) Calculations of cyclohexanol, its anion, and the core-ionized species were obtained by using the following structural parameters: C–C = 1.535 Å, C–O = 1.421 Å, C–H = 1.095 Å, O–H = 0.958 Å, C–O–H = 110.25°. The ring carbon atoms were approximately tetrahedral with respect to their attached carbon and hydrogen atoms. The ring was fixed in a chair confor-mation with the hydroxyl group in an equatorial position. The C–C–O bond was 112.43°, distorted from tetrahedral geometry such that the acidic hy-drogen was bent away from the ring. The plane containing carbon 1 and the hydroxyl group was parallel to a plane containing carbon atoms 2, 3, 5, and 6.
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4362 *J. Am. Chem. Soc., Vol. 108, No. 15, 1986*

Siggel and Thomas

hydroxyl oxygen for the neutral and core-ionized species, using the equivalent-cores approximation for the latter to simulate a molecule with a core-ionized oxygen. The ab initio and CNDO results are in good agreement with each other, as can be seen in Table I, where relevant results are given. Only the results of the Gaussian 82 calculations are discussed further here. Details and further interpretation of these calculations will be presented elsewhere.[14]

We now consider the quantitative importance of the two factors V and R in determining the energy required to remove the acidic proton. Considering first the results given in Table I for phenol and cyclohexanol, we see that in the initial state, the potential at the acidic proton, $\Phi(H)$, is -25.83 V for phenol and -27.03 V for cyclohexanol. Thus, ΔV is 1.20 eV, favoring the higher acidity of phenol. Upon removal of the proton, the electron that was largely localized on the proton is redistributed to the oxygen and the ring. The potential at the position formerly occupied by the proton, $\Phi(H^*)$, drops to -9.16 V for phenoxide and -10.78 V for alkoxide. Using eq 7 to calculate the relaxation contributions gives 8.34 eV for phenol and 8.13 eV for cyclohexanol. Thus, the acidity of phenol is favored by 0.21 eV. The acidity of phenol relative to that of cyclohexanol, ΔA, is calculated from these values and eq 9 to be -1.41 eV. Only 15% of this shift is due to differential rearrangement following ionization; the major part is due to the differences in the charge distribution in the initial state of the two molecules.

The calculations for acetic acid and 2-propanol indicate that the higher acidity (less positive) of acetic acid (ΔA, relative to the alcohol, is calculated to be -1.24 eV) is entirely due to the initial-state potential difference (1.62 eV using the 3-21G basis set and 1.72 eV using 3-21+G). The extra energy gained as the negative charge delocalizes over the anion actually favors the acidity of the alcohol by 0.38 (3-21G) to 0.46 (3-21+G) eV.[15]

Experimental Section

Most of the data necessary to determine experimental values of ΔV and ΔR are available. For the comparison between acetic acid and 2-propanol, we have used the results obtained by Mills, Martin, and Shirley.[16] They have measured the shift in the oxygen 1s ionization energy (acetic acid relative to 2-propanol) to be 1.55 eV.

To provide experimental values of ΔI for phenol and cyclohexanol, we have measured the oxygen 1s ionization energies for these compounds using standard procedures that are described elsewhere.[6,8] The oxygen 1s ionization energies are 539.23 (5) eV for phenol (average of 3 measurements) and 538.35 (5) eV for cyclohexanol (average of 2 measurements). The shift in ionization energy of the aromatic compound relative to the saturated one is, therefore, 0.88 (7) eV.

Gas-phase acidities have been reported for acetic acid (15.11 eV)[17] and for 2-propanol (16.22 eV).[18] Thus, ΔA for acetic acid relative to 2-propanol is -1.11 eV. Although a value of the gas-phase acidity of phenol is known (15.24 eV),[18] no corresponding value has been reported for cyclohexanol. However, the acidities of many saturated aliphatic alcohols have been determined.[18] As the number of carbon atoms is increased above five, the corresponding acidity increases by about 0.05 eV for each carbon added. This increase seems to be fairly insensitive to the position of the added methyl group. For example, sec-butyl alcohol and tert-butyl alcohol differ by the position of one methyl group; their acidities, however, are the same. We therefore assume that the gas-phase acidity of cyclohexanol is approximately the same as that of the six-carbon alcohol

3,3-dimethyl-2-butanol (16.08 eV).[18,19] With this value, we estimate the shift in gas-phase acidity, ΔA, of phenol relative to cyclohexanol to be -0.84 eV.[20]

Using these experimental values together with eq 10 and 11 gives a ΔV of 1.33 eV and a ΔR of -0.22 eV for acetic acid and a ΔV of 0.86 eV and ΔR of -0.02 eV for phenol. Although these values are somewhat lower than those calculated theoretically, the essential conclusion is the same: the values of ΔR are small and the difference in acidity arises principally from the initial-state charge distribution and only slightly or not at all from final-state charge rearrangement.

Since the oxygen core electron and the acidic proton are not at exactly the same location in the molecule, it is not obvious that ΔV and ΔR will be the same for the two processes. The last 4 columns of Table I show theoretical values of ΔV and ΔR at the oxygen site (before and after core ionization) and at the hydrogen site (before and after removal of the proton). The changes at the oxygen closely follow those at the hydrogen. Experimentally, Smith and Thomas[8] found that ΔV for the core ionization of oxygen is 1.1 times ΔV for removal of the acidic proton. They assumed a similar ratio for ΔR. With these relationships, the values of ΔV and ΔR derived from the experimental data are essentially no different from those given above.

Conclusions

From these observations, the following picture has emerged. Very little of the higher acidity of acids results from greater stabilization of the anion. Most of the difference between the acidity of alcohols and acids arises from the initial-state charge distribution, which leads to a potential at the proton that is less attractive in acids than in alcohols.

The differences in initial-state potential may arise from a variety of sources. In acetic acid, the carbonyl oxygen is more electronegative than the methyl group that it replaces in 2-propanol. In both acetic acid and phenol, resonance structures favor transfer of electrons from the π orbitals of the hydroxyl oxygen to those of either the carbonyl group or the aromatic ring. The carbon to which the hydroxyl group is attached is sp^2 hybridized in acetic acid and phenol and is, therefore, more electronegative than the sp^3 hybrid of the alcohols. All of these factors lead to electron withdrawal from the vicinity of the acidic hydrogen and to a more positive potential at this location.

The surprising result of these and related[21] investigations is that there is very little difference in final-state charge rearrangement between the acids and alcohols or, more generally, between molecules with double bonds and those without.[21] Theoretical investigations[21] indicate that the carbon skeletons of the molecules with double bonds are, indeed, more polarizable than the skeletons of comparable saturated molecules. Compensating this, however, is additional polarizability due to the electrons associated with the extra hydrogens of the saturated molecules. The net polarization is, therefore, nearly the same for both kinds of molecules when the hydroxyl proton is removed.

Measurements of core-ionization and Auger energies for haloethanes, haloethenes, cyclohexyl halides, and halobenzenes support these conclusions.[21] In each case, the potential at the substituent or heteroatom in the aromatic or unsaturated system is more positive than the potential at the corresponding atom in the saturated system, indicating initial-state delocalization of charge from the heteroatom to the molecule with double bonds. Furthermore, there is almost no difference between the relaxation

(15) The calculations reported here have been done with geometrically unrelaxed anions. To consider the effect of geometric relaxation, we have done an additional set of calculations in which the geometry of the anion was optimized. Acidities were then taken to be the difference between the total energies of the neutral molecule and corresponding anion. The relative acidities resulting from these calculations are -1.87 eV (3–21G) and -1.65 eV (3-21+G). With use of eq 9, these were combined with values of $\Delta V(H)$ (Table I) to give values of ΔR of 0.25 eV (3-21G) and -0.07 eV (3-21+G). The conclusions are unchanged: The relative acidities of acetic acid and 2-propanol are determined by the initial-state potential. The results involving geometric relaxation of the anion will be discussed in more detail in a further paper, ref 14.

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(19) This assumption is further supported by our measurement of the oxygen 1s ionization energy of 3,3-dimethyl-2-butanol as 538.36 (5) eV (average of two measurements), which is within 0.01 eV of the corresponding value for cyclohexanol.

(20) The gas-phase acidities used here are the enthalpy changes for removing a proton from the free, neutral molecule. From a chemical point of view, the more significant quantity is probably the change in the Gibbs free energy, which differs from the enthalpy change by $T\Delta S$. According to Bartmess et al. (ref 18), the principal contribution to ΔS is the entropy of the free hydrogen ion, which is the same for all acids. The variation in ΔS is only a few cal·deg^{-1}·mol^{-1} for a wide range of acids. The contribution of the $T\Delta S$ term to the relative acidity is, therefore, about 1 kcal·mol^{-1}, or 0.05 eV, and can be ignored in our considerations. The theoretical quantities calculated here are the changes in internal energy for proton removal. These differ from the enthalpy changes by RT, which cancels when we consider relative acidities.

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energies for the two systems, indicating that the aromatic compounds and alkenes are no more polarizable than alkanes with similar structures.

Appendix

We present here a quantum-mechanical derivation of eq 9, which describes the acidity in terms of an initial-state potential, V, and a final-state relaxation, R. The treatment given here is rigorous within the limits of the Born–Oppenheimer approximation. From this, we develop a quantum-mechanical derivation of eq 7, which is valid within somewhat narrower limits.

The gas-phase acidity is the difference between the total energy of the anion, E_a, plus that of a proton at infinity, which is zero, and the total energy of the neutral molecule, E_m. Thus

$$A = E_a - E_m \tag{12}$$

We can express this relationship quantum mechanically as

$$A = \langle \psi_a | \hat{H}_a | \psi_a \rangle - \langle \psi_m | \hat{H}_m | \Psi_m \rangle \tag{13}$$

where $\hat{H}_a$ and $\hat{H}_m$ are the Hamiltonian operators for the anion and molecule and ψ_a and ψ_m are the corresponding electronic eigenfunctions. $\hat{H}_a$ differs from $\hat{H}_m$ in that the anion has one fewer proton than the neutral species, and in that the nuclei are in the appropriate positions for the anionic ground state for $\hat{H}_a$ and for the neutral ground state for $\hat{H}_m$.

We introduce a hypothetical intermediate anionic state, in which the acidic proton has been removed but the remaining nuclei are in the positions appropriate to the molecular ground state. This is thus a geometrically unrelaxed configuration. We designate the Hamiltonian of this state as $\hat{H}_i$, its eigenfuncation as ψ_i, and its energy as

$$E_i = \langle \Psi_i | \hat{H}_i | \psi_i \rangle \tag{14}$$

Finally, we consider an energy, E', given by

$$E' = \langle \psi_m | \hat{H}_i | \psi_m \rangle \tag{15}$$

which is the energy of a state of the anion that is both geometrically and electronically unrelaxed.

We now rewrite eq 12 as

$$A = E_a - E_i + E_i - E' + E' - E_m$$
$$= \Delta E_3 + \Delta E_2 + \Delta E_1 \tag{16}$$

and note that

$$E' - E_m = \Delta E_1 = \langle \psi_m | \hat{H}_i | \psi_m \rangle - \langle \psi_m | \hat{H}_m | \psi_m \rangle$$
$$= \langle \psi_m | \hat{H}_i - \hat{H}_m | \psi_m \rangle \tag{17}$$

$$E_i - E' = \Delta E_2 = \langle \psi_i | \hat{H}_i | \psi_i \rangle - \langle \psi_m | \hat{H}_i | \psi_m \rangle \tag{18a}$$

$$E_i - E' = \Delta E_2 = \langle (\psi_i - \psi_m) | \hat{H}_i | (\psi_i - \psi_m) \rangle \tag{18b}$$

$$E_a - E_i = \Delta E_3 = \langle \psi_a | \hat{H}_a | \psi_a \rangle - \langle \psi_i | \hat{H}_i | \psi_i \rangle \tag{19}$$

From eq 17 we can see that ΔE_1 depends only on initial-state properties of the molecule. The difference $\hat{H}_i - \hat{H}_m$ reflects the change in Hamiltonian because a proton has been removed, without any other geometric changes. This difference is given by the expression

$$\hat{H}_i - \hat{H}_m = \sum_j \frac{1}{r_{Hj}} - \sum_\alpha \frac{Z_\alpha}{R_{H\alpha}} \tag{20}$$

Here, r_{Hj} is the distance between electron j and the site of the acidic proton; the first sum goes over all electrons. Z_α is the nuclear charge of nucleus α and $R_{H\alpha}$ is the distance between this nucleus and the site of the acidic proton. The second sum goes over all nuclei except the acidic proton.

The right-hand side of eq 20 is readily recognizable as the negative of the potential at the site of the acidic proton. Substituting eq 20 into eq 17 gives $\Delta E_1 = -\langle V \rangle$, which is the leading term of eq 4 and 9.

ΔE_2 is the change in energy resulting from the relaxation of the electrons in response to the disappearance of the proton. By the variational theorem, the second term on the right-hand side of eq 18a is greater than the first, so ΔE_2 is negative. We set it equal to $-R'$, where R' accounts for part of the relaxation energy of eq 9.

In eq 19, the term $\langle \psi_a | \hat{H}_a | \psi_a \rangle$ gives the energy of the ground state of the anion. The second term, which involves a different Hamiltonian for the same many-body system, must give a higher energy. ΔE_3 is, therefore, also negative and is represented by $-R''$.

Thus we have

$$A = -V - R' - R'' = -V - R \tag{21}$$

and

$$\Delta A = -\Delta V - \Delta R \tag{9}$$

V represents the potential at the proton in the neutral molecule and is an initial-state property. R represents the change in energy because of geometric and electronic relaxation and is a final-state property.

From electronic structure calculations we can calculate values for V, R', and R''. To first, order, these are -25 to -27, 9, and 0.1 to 0.6 eV, respectively. We might anticipate that the third of these, which is small, could be ignored in comparisons of different acids. This is probably a valid conclusion when we consider acids with similar structures in the vicinity of the acidic hydrogen (as in comparing carboxylic acids that have different substituents). Our theoretical calculations indicate that this term cannot be ignored in the comparison of carboxylic acids with alcohols but that it is not significant enough to change our overall conclusions.

Equation 7 can be derived following a procedure given by Davis and Rabalais,[2] who used the Hellmann–Feynmann theorem to investigate the energy changes when an electron is removed or a proton added to a molecule. Their treatment is easily modified for removal of a proton. In their analysis, the proton is "removed" by letting its charge, Z, go continuously to zero. If there is no geometric relaxtion during this process, then the energy needed to remove the proton is given by

$$A = \int_1^0 \langle \psi(Z) | V | \psi(Z) \rangle \, dz \tag{22}$$

where V is the potential at the site of the proton and $\psi(Z)$ is the electronic wave function. Because the electrons relax as the proton charge is lowered, ψ is dependent on Z. Rewriting the expectation value in eq 22 as $\langle V(Z) \rangle$, expanding in Taylor series, and integrating we have

$$A = -\langle V(1) \rangle + \frac{1}{2} \frac{d \langle V(Z) \rangle}{dZ} \bigg|_{Z=1} + \dots \tag{23}$$

Assuming that $\langle V(Z) \rangle$ is linear in Z gives

$$A = -\langle V(1) \rangle + \frac{1}{2} (\langle V(1) \rangle - \langle V(0) \rangle) \dots \tag{24}$$

Comparing this with eq 4, we see that

$$\alpha = \langle V(0) \rangle - \langle V(1) \rangle \tag{25}$$

which is the quantum mechanical equivalent of eq 7, with $q = 1$.