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The Anomalous Gas-Phase Acidity of Formic Acid. Importance of Initial-State Polarization

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Abstract: In the gas phase, carboxylic acids generally become stronger acids (ΔH°_{acid} decreases) as the size of the alkyl group increases. The acidity of formic acid is anomalous; it is a stronger acid (smaller ΔH°_{acid}) than acetic, propionic, and butyric acids. From comparisons of gas-phase acidities with core-ionization energies, and from ab initio electronic structure calculations, it is shown that this anomaly arises because replacement of hydrogen by an alkyl group in a carboxylic acid gives rise to an unusually high change in the potential at the acidic proton in the neutral acid and a smaller change in the relaxation that occurs when the proton is removed. Analysis of the charge distributions in these molecules (obtained from Integrated Bader Populations) shows that there is a significant charge transfer from the alkyl group to the carboxy group—especially to the carboxy carbon.

In general carboxylic acids, R-COOH, where R is a straight-chain saturated alkyl group, in the gas phase become stronger acids as the size of the alkyl group increases.[1,2] In other words, it becomes easier to remove the acidic proton as the size and, hence, polarizability of the alkyl group increases. This trend is similar to that seen in alcohols, where their acidity is directly related to their size—the larger the alcohol, the stronger the acid. This trend has been attributed to the greater ability of larger alkyl groups to accommodate negative charge in the anion.[3]

Formic acid, however, is anomalous in that it is a stronger acid (and, correspondingly, has a smaller ΔH°_{acid}) than several other carboxylic acids that contain groups more polarizable than hydrogen; such acids include acetic, propionic, and butyric acids.[2] The anomalous acidity of formic acid has been attributed to a large inductive effect in the neutral un-ionized acids, and it has been suggested that hydrogen is more electron withdrawing than methyl when attached to a carbonyl group.[4] This interpretation, however, appears to be in conflict with other views about substituent effects. For instance, Pearson has concluded from the properties of alkanes that hydrogen must have an electronegativity close to that of methyl.[5] An analysis by Taft and Topsom[6] shows that the electronegativity difference between hydrogen and an alkyl group (expressed as a Hammett substituent parameter, σ_χ) is small and furthermore that the effect of the electronegativity of a substituent in the position of the hydrogen or alkyl group is also small ($\rho_\chi \approx 0$). According to Taft and Topsom, the significant difference between hydrogen and alkyl groups is in the higher polarizability (σ_α) of the latter. It is not immediately apparent how the polarizability of the substituent can lead to the postulated inductive effect.

In considering this question further, it is useful to divide the factors affecting the acidity into two categories: those affecting the neutral un-ionized molecule and those affecting the ability of the ion to accommodate the negative charge. These are known as initial- and final-state effects, respectively. The energies involved in these two effects have been shown to have a clear theoretical definition and can be experimentally determined by combining gas-phase acidities with hydroxy-oxygen core-ionization energies.[4,7] The relationship between acidity and core ionization is that each is the energy associated with the removal of one unit of localized charge (positive or negative, respectively). The relevant expressions are

$$\Delta A = -\Delta V - \Delta R \qquad (1)$$

and

$$\Delta I = \Delta V - \Delta R \qquad (2)$$

where A is the gas-phase acidity, which is the enthalpy change for the reaction $ROH \rightarrow RO^- + H^+$, ΔA is the difference in the gas-phase acidities between two molecules, ΔI is the difference in core-ionization energies, ΔV is the initial-state potential shift, and ΔR is the final-state relaxation energy difference. The initial-state potential, V, is the potential energy of a unit positive charge at the site from which the proton or the electron is to be removed. The final-state relaxation energy, R, is the stabilization energy of the final ion resulting because of rearrangement of valence electrons in response to the removal of the proton or electron. Equations 1 and 2 can be combined to give expressions for the initial- and final-state shifts, each in terms of experimentally measured parameters.[8]

Table I. Gas-Phase Acidities (ΔH°_{acid}) of Carboxylic Acids[a]

acid	formula	ΔH°_{acid} kcal mol^{-1}	ΔH°_{acid} eV
formic	$HCOOH$	345.2	14.97
acetic	CH_3COOH	348.5	15.11
propionic	CH_3CH_2COOH	347.3	15.06
butyric	$CH_3CH_2CH_2COOH$	346.5	15.03

[a] Taken from ref 1. The absolute uncertainty is 2 kcal mol^{-1}, but the relative uncertainty is 0.2 kcal mol^{-1}.

Table II. Experimental Gas-Phase-Acidity (ΔH°_{acid}) Shifts. Hydroxy-Oxygen Core-Ionization-Energy Shifts, Initial-State Potential-Energy Differences, and Final-State Relaxation Differences in Carboxylic Acids (All in eV)

acid	ΔA[a]	ΔI	ΔV	ΔR
acetic	0	0	0	0
propionic	−0.05	−0.11[b]	−0.03	+0.08
butyric	−0.08	−0.14[c]	−0.03	+0.11
formic	0	0	0	0
acetic	+0.14	−0.55[b]	−0.35	+0.21
propionic	+0.09	−0.66[b]	−0.38	+0.29
butyric	+0.06	−0.69[c]	−0.38	+0.32

[a] Taken from ref 1. [b] Taken from ref 9. [c] This study.

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(8) Core ionization is a vertical process and, therefore, only electronic relaxation is involved. Proton removal, however, is an adiabatic process where both electronic and geometric relaxation occur. In our model we are assuming that the relaxation accompanying core ionization is equal to the relaxation accompanying proton removal. This approximation is justified because the geometric relaxation is small compared with the electronic relaxation that accompanies proton removal. See ref 20 and footnote 15 of ref 7.

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Experimental Results

Gas-Phase-Acidity Shifts. The gas-phase acidities of formic, acetic, propionic, and butyric acids are given in Table I. With the exception of formic acid, the acids become stronger ($\Delta H^\circ_{\mathrm{acid}}$ decreases) with increasing size—by 0.05 eV between acetic and propionic acids and by 0.03 eV between propionic and butyric acids. The amount by which the acids become stronger, or $\Delta H^\circ_{\mathrm{acid}}$ becomes smaller, as the alkyl chain is lengthened decreases with each addition of a methylene group. This result is consistent with the notion that polarization effects decrease with distance.

Oxygen Core-Ionization-Energy Shifts. We have used the results obtained by Mills, Martin, and Shirley for the hydroxy-oxygen core-ionization-energy shifts between formic, acetic, and propionic acids.[9] Their results are presented in Table II. To provide an experimental value of ΔI for butyric acid, we have determined the oxygen 1s ionization energies for propionic and butyric acids from the measured oxygen 1s ionization energies of their methyl esters according to the method described by Siggel and Thomas.[10] The experimental measurements were made on the Oregon State University cylindrical-mirror analyzer[11] using standard procedures that are described elsewhere.[4,12] The measured oxygen 1s ionization energies are 539.33 (5) and 537.76 (4) eV for methyl propionate and 539.30 (3) and 537.73 (3) eV for methyl butyrate. (The two numbers given for each molecule correspond to the methoxy and carbonyl oxygen atoms, respectively).

Using the linear correlation between oxygen core-ionization of alcohols and carboxylic acids and those of the corresponding methyl ethers and esters {$I(\mathrm{R{-}O{-}Me}) = 0.86826 \times I(\mathrm{R{-}O{-}H}) + 70.505$}[10] we estimate hydroxy-oxygen core-ionization energies of 539.96 (5) and 539.93 (3) eV for propionic and butyric acids, respectively. The predicted value for propionic acid differs by 0.08 eV from the experimental value of 540.04 (5) eV reported by Mills, Martin, and Shirley.[9] Although the discrepancy between these two numbers is large, it is approximately within the combined uncertainty of the two values. The ionization-energy shifts reported by each group are probably more accurate because of cancellation of systematic errors that differ between the two laboratories.

Initial- and Final-State Shifts. The experimental gas-phase-acidity shifts, hydroxy-oxygen core-ionization-energy shifts, initial-state shifts, and final-state relaxation energy shifts for the first four carboxylic acids are given in Table II. The initial- and final-state shifts have been determined from the acidities and core-ionization energies using eqs 1 and 2. The results, presented in Table II, have been divided into two groups. The first group gives the shifts for typical carboxylic acids; these are given relative to acetic acid. The second group shows the anomalous shifts that result when formic acid is included. These two groups of experimental results are discussed in the following two sections. In order to facilitate the discussion, we use the notation "acetic/formic acid" to mean "acetic acid relative to formic acid" and "propionic/acetic acid" to mean "propionic acid relative to acetic acid", etc.

General Acidity Trend. The numbers in the upper part of Table II show that as the size, and polarizability, of the alkyl group increases, both ΔA and ΔI decrease; it, thus, becomes easier to remove both the proton and the core electron. The amount by which the core-ionization energy decreases (ΔI) is about twice that by which the acidity decreases (ΔA) for a given increase in size.

The main contribution to the differences in gas-phase acidities and hydroxy-oxygen core-ionization energies for acetic and larger carboxylic acids is final-state relaxation; the magnitude of the initial-state shift is less than half that of the relaxation shift. The dominance of the relaxation term is consistent with previous studies where the main difference between the molecules is polarizability. For example, Aitken et al.[12] used measurements of core-ionization and Auger energies to determine ΔV and ΔR for a series of chlorine-containing compounds. Their results, summarized in Table III, show that ΔR is larger in magnitude than ΔV and increases with the size of the alkyl group. Similar results are seen in Table III for straight-chain alcohols (where the values of ΔV and ΔR have been determined from values of $\Delta H^\circ_{\mathrm{acid}}$[2] and core-ionization energies[9]) and for ethers and esters[10] (where the values come from ab initio calculations). Each of the four examples given in Table III show the effect of increasing the chain length of a substituent (e.g. replacement of $-H$ by $-CH_3$, $-CH_3$ by $-CH_2CH_3$, and $-CH_2CH_3$ by $-CH_2CH_2CH_3$). Although Table III is limited to straight-chain substituents, the same conclusions are reached for branched systems (e.g. successive replacement of hydrogen atoms ($-H$) that are attached to a given center by methyl groups ($-CH_3$)). Four such examples are given in Table IV; these include alcohols and chlorine-, sulfur-, and germanium-containing compounds.

Table III. Initial- and Final-State Shifts (eV) as a Function of Substituent Chain Length

molecule	formula	ΔV	ΔR
hydrochloric acid[a]	HCl	0	0
methyl chloride[a]	CH_3Cl	−0.41	+0.71
ethyl chloride[a]	CH_3CH_2Cl	−0.44	+1.02
1-propyl chloride[a]	$CH_3CH_2CH_2Cl$	−0.49	+1.07
water[b]	HOH	0	0
methanol[b]	CH_3OH	−0.19	+0.60
ethanol[b]	CH_3CH_2OH	−0.27	+0.83
1-propanol[b]	$CH_3CH_2CH_2OH$	−0.28	+0.90
methanol[c]	$HOCH_3$	0	0
dimethyl ether[c]	CH_3OCH_3	−0.17	+0.70
ethyl methyl ether[c]	$CH_3CH_2OCH_3$	−0.29	+0.86
formic acid[c]	$HOOCH$	0	0
methyl formate[c]	CH_3OOCH	−0.46	+0.73
ethyl formate[c]	CH_3CH_2OOCH	−0.63	+0.89

[a] Taken from ref 12. [b] The initial- and final-state shifts were determined using eqs 1 and 2 together with gas-phase acidities ($\Delta H^\circ_{\mathrm{acid}}$) from ref 2 and oxygen core-ionization energies from ref 9. [c] Taken from ref 10.

Table IV. Initial- and Final-State Shifts (eV) for Branched Systems

formula	ΔV	ΔR
CH_3OH[a]	0	0
$(CH_3)CH_2OH$[a]	−0.08	+0.23
$(CH_3)_2CHOH$[a]	−0.15	+0.39
CH_3Cl[b]	0	0
$(CH_3)CH_2Cl$[b]	−0.03	+0.31
$(CH_3)_2CHCl$[b]	−0.12	+0.52
$(CH_3)_3CCl$[b]	−0.25	+0.63
SH_2[c]	0	0
$(CH_3)SH$[c]	+0.17	+0.72
$(CH_3)_2S$[c]	+0.05	+1.20
GeH_4[d]	0	0
$(CH_3)GeH_3$[d]	−0.16	+0.30
$(CH_3)_4Ge$[d]	−0.33	+0.94

[a] The initial- and final-state shifts were determined using eqs 1 and 2 together with gas-phase acidities ($\Delta H^\circ_{\mathrm{acid}}$) from ref 2 and oxygen core-ionization energies from ref 9. [b] Taken from ref 12, where the values were derived from experimental chlorine 2p core-ionization energies and chlorine KLL Auger kinetic energies. [c] The initial- and final-state shifts were determined using sulfur 1s ionization energies and sulfur KLL Auger kinetic energies from Carroll et al. (Carroll, T. X.; Ji, D.; MacLaren, D. C.; Thomas, T. D. *J. Electron Spectrosc. Relat. Phenom.*, **1987**, *42*, 281) together with equations that are given in ref 12. [d] Taken from ref 12, where the values were derived from experimental germanium 3d core-ionization energies and Auger kinetic energies from Perry and Jolly (Perry, W. D.; Jolly, W. L. *Chem. Phys. Lett.* **1973**, *23*, 529).

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Final-state relaxation always lowers the energy required for a given process, and therefore has the effect of making the acid stronger and core ionization easier. A negative initial-state shift (ΔV) decreases the core-ionization-energy shift (ΔI), but increases the gas-phase-acidity shift (ΔA). This result makes sense from an electrostatic point of view; the more negative the electrostatic potential at the hydroxy oxygen, the easier it is to remove the core electron and the harder it is to remove the acidic proton. For molecules in which ΔV is negative and ΔR is positive (i.e. for most of the examples given in Tables III and IV), the initial- and final-state contributions toward gas-phase-acidity shifts oppose one another; ΔV increases ΔA while ΔR lowers ΔA. With respect to core ionization, both ΔV and ΔR lower ΔI. That the magnitude of ΔI is larger than the magnitude of ΔA is a reflection of these differences.

Although the effects seen in Tables III and IV are qualitatively similar to those for the carboxylic acids given in Table II, we note two important differences. First, the relaxation energies shown in Tables III and IV are, in general, significantly larger than those in Table II. This difference arises because the effect of a polarizable group falls off rapidly with distance. For all of the compounds shown in Table III and IV, the polarizable group is attached directly to the center from which charge is removed; for the carboxylic acids the polarizable group is remote from this center (the hydroxy oxygen). Second, the magnitudes of ΔV shown in the last 4 lines of Table II (for carboxylic acids relative to formic acid) are comparable to the largest values shown in Tables III and IV. Thus ΔV is a relatively more important effect and ΔR a relatively less important effect for the carboxylic acids than for the other compounds.

The Anomalous Gas-Phase Acidity of Formic Acid. The initial- and final-state contributions to the acidity difference between formic and acetic acids are given in the lower part of Table II. The signs of both ΔV and ΔR are consistent with the general trends discussed above. The magnitudes of ΔV and ΔR, however, are much larger for acetic/formic acid than for propionic/acetic acid or butyric/acetic acid. Furthermore, and perhaps most important, are the relative magnitudes of ΔV and ΔR for acetic/formic acid. Unlike the general trends discussed in the preceding section, ΔV is larger in magnitude than ΔR.

The large final-state shift, ΔR, for acetic/formic acid is as expected. The replacement of the relatively nonpolarizable hydrogen substituent by a polarizable methyl group results in a large contribution from ΔR. Replacement of the polarizable methyl group (in acetic acid) by a larger, and more polarizable, alkyl group (such as ethyl or *n*-propyl) results in much smaller contributions from ΔR. However, as noted above, ΔR for the carboxylic acids is less than for the other types of compounds.

The large initial-state shift, ΔV, is surprising since the electronegativities of hydrogen and methyl are thought to be about the same;[5,6] as previously discussed, only small initial-state shifts are expected when two systems differ mainly in polarizability. However, this result is consistent with the data given in Table III. These results show that the replacement of a relatively nonpolarizable hydrogen by a more polarizable methyl group invariably leads to a significantly more negative ΔV.

The carboxy group in carboxylic acids is highly polar; the oxygens possess high negative charges and the carbon and hydrogen are highly positive.[13,14] The carboxy group is thus expected to polarize other substituents in such a way so as to cause the electrostatic potential at the hydroxy hydrogen to become more negative. This effect will be largest when a relatively nonpolarizable group, such as hydrogen, is replaced by a polarizable group such as an alkyl group. In the case of the other examples shown in Table III, a similar polarization of the methyl group is produced by an electronegative center.

The important, and surprising, result is that the initial-state shift dominates over final-state relaxation for acetic/formic acid. For the eight sets of molecules shown in Tables III and IV, the magnitude of ΔR is always larger than the magnitude of ΔV whereas for the acids shown in the lower part of Table II the reverse is true. The anomalous gas-phase acidity of formic acid is a consequence of the anomalous dominating initial-state effect.

Table V. Theoretical[a] Gas-Phase-Acidity ($\Delta H^\circ_{\text{acid}}$) Shifts, Hydroxy-Oxygen Core-Ionization-Energy Shifts, Initial-State Potential-Energy Differences, and Final-State Relaxation Differences in Carboxylic Acids (All in eV)

acid	ΔA	ΔI	ΔV	ΔR
acetic	0	0	0	0
propionic	+0.01	−0.10	−0.05	+0.04
formic	0	0	0	0
acetic	+0.20	−0.49	−0.35	+0.15
propionic	+0.21	−0.59	−0.40	+0.19

[a] Results were obtained using the Gaussian 82[15] and 86[16] series of ab initio programs. Results for formic acid and formate ion were obtained at the RHF/6-31+G*//6-31+G* level: results for acetic acid, acetate ion, propionic acid, and propionate ion were obtained at the RHF/6-31+G*//6-31G* level. The initial-state potentials were given directly by the ab initio program. The theoretical acidities ($\Delta H^\circ_{\text{acid}}$) were determined as the difference in total energy between the anion and the neutral molecule. The binding-energy shift and final-state relaxation differences were calculated using ΔV and ΔA together with eqs 1 and 2.

Theoretical Results

We now consider the results of ab initio electronic structure theory to gain further insight into the factors that contribute to the initial- and final-state shifts. Topics to be addressed include an analysis of the atomic populations and population changes accompanying deprotonation and the relative contribution of polarization and electron transfer between the carboxy group and the rest of the molecule.

Initial- and Final-State Effects from ab Initio Theory. We have used ab initio electronic structure theory (Gaussian 82[15] and Gaussian 86[16] as the restricted Hartree–Fock level with the 6-31G* and 6-31+G* basis sets) to obtain the electronic charge distributions in formic, acetic, and propionic acids and the anions that are obtained by removing the acidic proton from these acids.

Optimized geometries are used for each molecule and ion. The geometries of formic acid and formate ion were obtained using the 6-31+G* basis set as reported in a previous study.[14] The geometries of acetic and propionic acids and their anions were obtained using the 6-31G* basis set. It was desired that the lowest energy conformation of each species be used. Conformational studies have been reported for acetic acid[17,18] and propionic acid;[17,19] we have used the lowest energy conformations given by these studies. In acetate ion, the rotational barrier for the methyl group is small (~0.01 eV using the 3-21+G basis set);[20] we have used the slightly higher energy conformation because of its higher symmetry. To determine the lowest energy conformation of propionate ion, we optimized the geometries of four rotamers using the 6-31G* basis set. The conformations used in this theoretical study are shown in Figure 1. The optimized geometries and total energies of all species discussed in this theoretical study are given in accompanying Supplementary Material.

We have calculated acidities, or $\Delta H^\circ_{0,\text{acid}}$, and initial-state potentials from the results of the ab initio calculations using the

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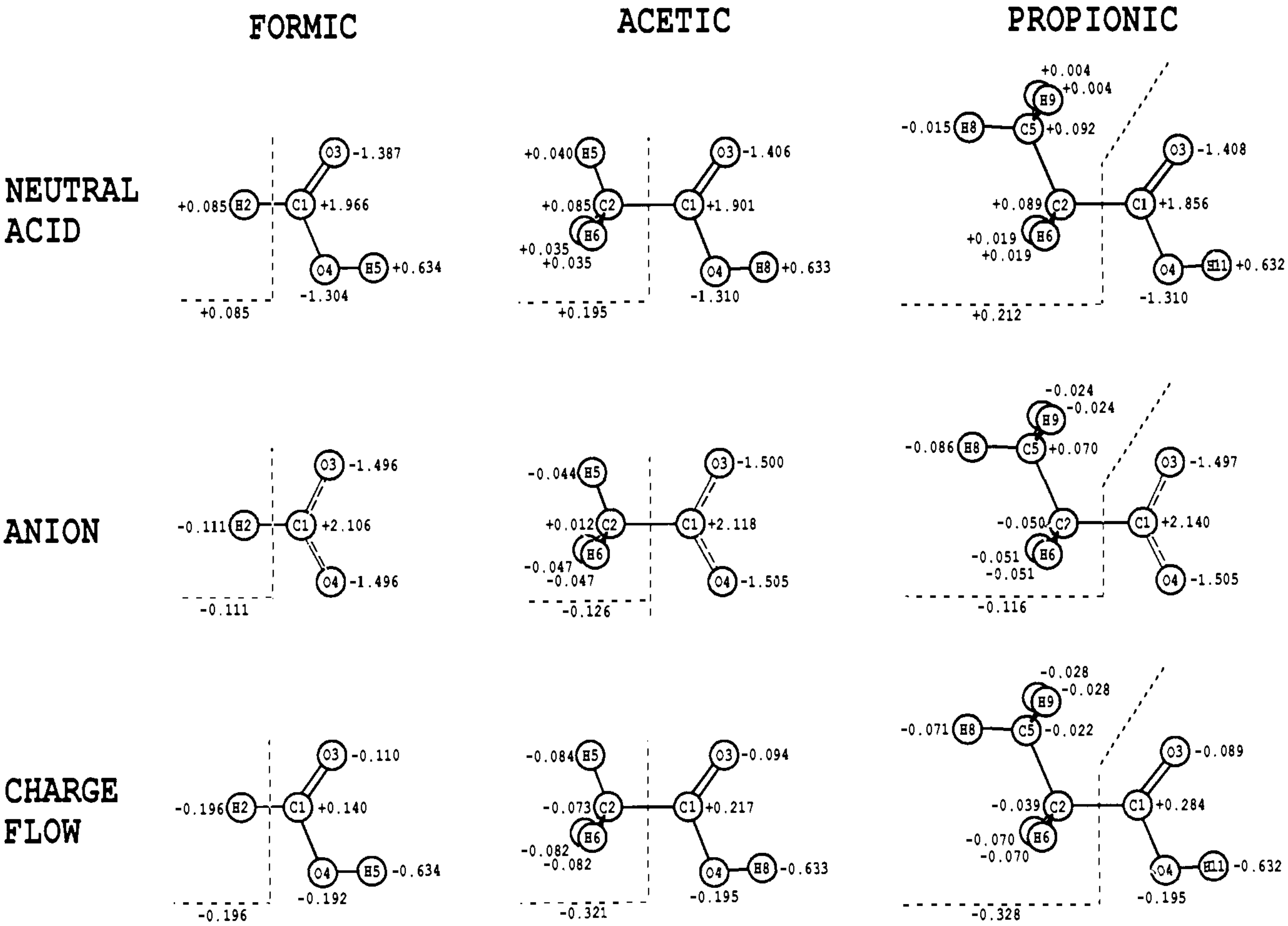

Figure 1. Atomic charges for carboxylic acids and carboxylate anions and the charge flow that results when the acidic proton is removed from the acid. The sum of the atomic charges and charge changes associated with the atoms of the substituent group are given below the dashed line for each species. All values obtained from Integrated Bader Populations.

optimized geometries described above and the 6-31+G* basis set. The acidity, or $\Delta H^{\circ}_{0,\mathrm{acid}}$, is equal to (and determined by taking) the difference between the calculated total energies of the anion and the neutral molecule. The initial-state potential at the proton is calculated from the theoretical charge distribution and is given directly by the Gaussian 82 and 86 programs. These results are presented as shifts, propionic/acetic acid and acetic/formic acid, in Table V. Combining these data together with eqs 1 and 2 gives theoretical core-ionization-energy shifts and final-state relaxation-energy shifts.

Comparing the theoretical results in Table V with the experimental results in Table II shows that, except for the relative acidities of acetic and propionic acids, the theoretical results reproduce the experimental trends. This comparison gives us confidence that we adequately represent the molecules and ions at this level of theory. We now use the theoretical charge distributions to gain further insight into factors affecting the initial- and final-state contributions to the acidity shifts.

Atomic Charges. We have determined atomic charges from the theoretical charge densities given by the Gaussian 82 and 86 programs using the method developed by Bader and co-workers.[21] In this method, a set of partitioning surfaces divides the real three-dimensional electron-density distribution into atomic volumes, or basins. These surfaces start at a saddle point in the electron distribution between a pair of atoms and follow paths of steepest descent through the electron distribution. The electron populations that are obtained by integrating over the volumes defined by these surfaces are known as "Integrated Bader Populations" or IBP's. The net charge of the atom is given by the difference between the nuclear charge and the IBP.

Table VI. Integrated Bader Populations[a]

formic acid		acetic acid		propionic acid	
atom	IBP	atom	IBP	atom	IBP
C1	4.0337	C1	4.0993	C1	4.1441
O3	9.3866	O3	9.4063	O3	9.4085
O4	9.3041	O4	9.3097	O4	9.3101
H5	0.3657	H8	0.3674	H11	0.3678
H2	0.9148	C2	5.9146	C2	5.9111
		H6	0.9646	H6	0.9808
		H7	0.9646	H7	0.9808
		H5	0.9603	C5	5.9077
				H8	1.0152
				H9	0.9964
				H10	0.9964
total	24.0049	total	31.9868	total	40.0189
formate ion		acetate ion		propionate ion	
atom	IBP	atom	IBP	atom	IBP
C1	3.8939	C1	3.8823	C1	3.8605
O3	9.4963	O3	9.4999	O3	9.4972
O4	9.4963	O4	9.5049	O4	9.5052
H2	1.1112	C2	5.9876	C2	5.9504
		H6	1.0467	H6	1.0511
		H7	1.0467	H7	1.0511
		H5	1.0442	C5	5.9298
				H8	1.0862
				H9	1.0243
				H10	1.0243
total	23.9977	total	32.0123	total	39.9801

[a] In the acids, O3 is the carbonyl oxygen and O4 is the hydroxy oxygen.

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The IBP's for the atoms in formic, acetic, and propionic acids and their anions are given in Table VI. The atomic charges and atomic charge changes that result when the acidic proton is removed, as determined from the IBP's, are given in Figure 1. The group charges and charge changes for the substituents of the carboxy groups (i.e. hydrogen in formic acid and formate ion, methyl in acetic acid and acetate ion, and ethyl in propionic acid and propionate ion) are included. The following discussion refers to Figure 1.

The atomic charges for the equivalent oxygen and hydrogen atoms in the carboxy groups are essentially the same (within 0.02 e) among the three carboxylic acids shown. Similarly, the oxygen atomic charges in the anions are also essentially identical. It therefore follows that the charge flow into and out of the oxygen and hydroxy hydrogen basins upon deprotonation is also essentially the same. We found these results quite surprising. We had expected to find differences in the populations of these atoms in neutral formic and acetic acids corresponding to the large initial-state shift (ΔV), and differences in charge flow between these two systems corresponding to the observed final-state relaxation (ΔR). The similarity between acetic and propionic acids is more in agreement with our expectations.

What does contribute to the large initial-state shift between formic acid and acetic acid? Inspection of Figure 1 shows that the major difference in atomic populations occurs at the carboxy carbon, C1, and that the charges on the carboxy carbon atoms are all large and positive. This large, positive charge provides a very electronegative center that strongly polarizes the methyl substituent, with transfer of negative charge principally to the carboxy carbon. The IBP charge analysis shows that the carboxy carbon, C1, in acetic acid is more negative than in formic acid (by 0.065 e). To balance this, the methyl group in acetic acid is more positive than the substituent hydrogen in formic acid. Since the carboxy carbon (C1) is much closer to the hydroxy hydrogen than is the substituent to the hydroxy hydrogen, the contribution of the carboxy carbon charge toward the electrostatic potential at this hydrogen dominates over the substituent charge. Comparison of the carboxy carbon and substituent group charges in the three neutral acids shows that the high positive charge associated with the carboxy carbon is reduced as the size, and hence polarizability, of the alkyl group is increased. This is an example of the importance of polarizability on the initial state, an effect that has only recently been recognized.[10] This effect is particularly pronounced in carboxylic acids because of the high positive charge on the carboxy carbon.

We now ask what atoms or groups contribute to the final-state relaxation shift between formic acid and acetic acid. The 0.37 electron associated with the acidic proton in the neutral molecules will redistribute upon proton loss. This redistribution is reflected in the charge flow data presented in Figure 1. The results for formic acid show that the electrons that were originally localized on the hydroxy hydrogen spread to the periphery of the ion, thus minimizing the electrostatic repulsion. Differences in the charge flow between formic and acetic acids occur predominately at the carboxy carbon and in the substituent group. The methyl group in acetic acid accepts more of the excess charge (−0.125 e) than the substituent hydrogen in formic acid. These results are in agreement with a similar study on alcohols which found the oxygen populations to be constant (not affected by the alkyl group) and the negative charge to delocalize to the substituent's hydrogen atoms.[22] It is to be noted that the methyl group serves as a better electron donor than hydrogen in the initial state and as a better electron acceptor than hydrogen in the final state. This result is in keeping with the general notion that alkyl groups either accept or donate electrons as needed.[23] It is also to be noted that part of the electron redistribution involves transfer of electrons from the carboxy carbon to the periphery of the molecule. The carboxy carbons become more positive (lose electrons); the carboxy carbon in acetic acid gains more positive charge (0.077 e) than in formic acid. The greater redistribution of charge in acetic/formic acid upon deprotonation is consistent with the large, positive ΔR found experimentally.

Table VII. Monopole, Dipole, and Quadrupole Contributions (All in V) to the Electrostatic Potential at the Acidic Proton[a]

acid	basin	monopole	dipole	quadrupole	sum
formic acid	C1	+15.143	+1.396	+0.088	+16.626
	O3	−8.620	−0.604	+0.035	−9.189
	O4	−19.692	−0.488	+2.139	−18.041
	H5	−17.223	0.000	0.000	−17.223
	H2	+0.441	+0.118	+0.027	+0.586
	sum	−29.951	+0.421	+2.289	−27.242
	ΔV	0.000	0.000	0.000	0.000
acetic acid	C1	+14.691	+1.610	+0.030	+16.331
	O3	−8.938	−0.593	+0.039	−9.492
	O4	−19.803	−0.627	+2.327	−18.103
	H8	−17.313	0.000	0.000	−17.313
	C2,H5-7	+0.824	+0.294	+0.025	+1.143
	sum	−30.539	+0.684	+2.421	−27.435
	ΔV	−0.588	+0.263	+0.132	−0.193
acetic/ formic acid	C1	−0.452	+0.214	−0.058	−0.295
	O3	−0.318	+0.011	+0.004	−0.303
	O4	−0.111	−0.139	+0.188	−0.062
	H8	−0.090	0.000	0.000	−0.090
	R	+0.383	+0.176	−0.002	+0.557
	sum	−0.588	+0.263	+0.132	−0.193
	ΔV	−0.588	+0.263	+0.132	−0.193
propionic acid	C1	+14.347	+1.716	−0.015	+16.048
	O3	−8.960	−0.602	+0.045	−9.517
	O4	−19.811	−0.620	+2.369	−18.062
	H11	−17.327	0.000	0.000	−17.327
	C2 and 5, H6-10	+0.848	+0.332	+0.029	+1.209
	sum	−30.903	+0.826	+2.428	−27.649
	ΔV	−0.952	+0.405	+0.139	−0.407

[a] In the acids, O3 is the carbonyl oxygen and O4 is the hydroxy oxygen.

Electrostatic Potentials from the Bader Charge Analysis. The Bader partitioning of the molecule provides an approach by which we can see more quantitatively the effects of the charge distribution that have been discussed above. The Bader method gives not only a charge to be assigned to each atomic center but also atomic dipole and quadrupole moments for each atomic basin. These can be used together with standard electrostatic formulas to calculate the contributions of each moment of each basin to the potential at the acidic hydrogen. These contributions are summarized in Table VII, along with the shifts for these values for acetic/formic acid.

There are two problems with this approach. First, using only the first three moments of the charge distribution does not give an accurate picture of the effects of the charge distribution. For instance, the potential at the acidic hydrogen in formic acid calculated in this way is −27.2 V whereas that calculated analytically by the Gaussian 86 program from the wave functions is −25.1 V.[24] The discrepancy is presumably due to the neglect of octupole and higher terms. However, this is reasonably constant for the three molecules of interest and we expect some cancellation of errors from this source when we look at differences in the potential between different molecules.

A second problem is that although the Bader integration gives total molecular electronic populations within 0.1% of the correct value, these are still not sufficiently accurate. The total charge on the molecules and ions of interest differs from the actual charge

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[22] Stutchbury, J. C. J.; Cooper, D. L. *J. Chem. Phys.* **1983**, *79*, 4967.

[23] Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1969; p 80.

[24] In eqs 1 and 2, ΔV appears to have units of energy rather than units of potential. If V is expressed in V, its effect on the ionization energy, given in eV, is numerically equal to the potential.

by as much as ±0.02 e. The potential at the proton may be in error from this source by 0.1 to 0.2 eV and, since these appear to be random rather than systematic, the errors in the relative values of ΔV may be still larger. In spite of these difficulties, this analysis provides additional insight into the atomic contributions to the electrostatic potential shifts at the acidic proton.

First consider the total contributions of the monopole, dipole, and quadrupole moments to the electrostatic potentials at the acidic protons for formic and acetic acids. These numbers are given in the 6th and 13th rows of Table VII; the shifts, or differences, between these two sets of values are given in the 14th row (labeled ΔV). The monopole, or charge, contribution to ΔV is negative (−0.588 V) while the dipole and quadrupole contributions are both positive (+0.263 and +0.132, respectively). Therefore, it is the dominance of the charge contribution that produces the observed negative initial-state shift.

Second, consider the sum of each basin's monopole, dipole, and quadrupole contributions to the electrostatic potential at the acidic protons in formic and acetic acids. These values are given in the last column of Table VII. All carboxy group atoms contribute a negative shift to ΔV for acetic/formic acids [C1 (−0.295), O3 (−0.303), O4 (−0.062), H8–5 (−0.090)]; the substituent shift is positive (+0.557).

Now consider the individual monopole, dipole, and quadrupole contributions for each basin. Looking first at contributions from the basin quadrupole moments, we find that the only significant contribution from these to the potential at the hydrogen is from the hydroxy oxygen (O4). It is positive and becomes more so (+0.188 V) as the hydrogen is replaced with a methyl group. For the dipole moments, the hydroxy oxygen produces the only negative shift (−0.139). For the monopole, or charge contributions, all atoms contribute a negative shift except for the substituent. The charge on the methyl group in acetic acid is more positive than that on the substituent hydrogen in formic acid; the negative charge contributions arise from the electrons that have been transferred from the methyl group to the atoms of the carboxy group. The largest contributions arise from C1, the carboxy carbon, −0.45 V (because the charge there has become more negative by a relatively large amount, −0.07 e), and the carboxy oxygen, −0.32 V (because of its close proximity to the hydroxy oxygen). The charge and dipole contributions of the methyl group are positive; the quadrupole contribution is negligible. Thus, the methyl group makes its effect felt by contributing electrons to the polar carboxy group rather than through induction of a dipole moment (polarization) on the methyl group.

Conclusions

These experimental results show the influence of initial- and final-state effects on the relative gas-phase acidities of a series of carboxylic acids. The results for acetic, propionic, and butyric acids are as expected; the shift in final-state relaxation, relative to acetic acid, for these molecules is large and positive and the shift in initial-state is relatively small and negative. This is in keeping with the results of previous studies where molecules that differed primarily in polarizability were studied.

The anomalous gas-phase acidity of formic acid is attributed to a large, and dominating, initial-state potential shift. This is the reverse of what one might expect and the reverse of what is seen for other systems when hydrogen is replaced by a methyl group. Two factors contribute to this reversal. The effect of the methyl group on the initial-state potential is unusually large because the methyl group is attached to a very electronegative center—the carboxy carbon—and in the initial state, the methyl group is highly polarized and contributes electrons to the carboxy carbon. Relaxation effects are reduced from what is seen for other systems because the methyl group is relatively remote from the site where the positive charge is removed (from the hydroxy group).

The charge-distribution calculations show that the main effect of the alkyl substituent in the neutral acids is to reduce the high positive charge imposed on the carboxy carbon by the electronegative oxygen atoms through transfer of electrons to the carboxy group, and to accept electrons from the carboxy group during the relaxation to the final state.

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Registry No. Formic acid, 64-18-6; acetic acid, 64-19-7; propionic acid, 79-09-4; butyric acid, 107-92-6; methyl propionate, 554-12-1; methyl butyrate, 623-42-7; germane, 7782-65-2; formate anion, 71-47-6; acetate anion, 71-50-1; propionate anion, 72-03-7.

Supplementary Material Available: Listing of optimized geometries of formic acid, formate ion, acidic acid, acetate ion, and propionic acid together with the RHF-SCF energies (5 pages). Ordering information is given on any current masthead page.

An ab Initio Theoretical Reaction Path Study of the Cation Radical Diels–Alder Reaction

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Abstract: The theoretical reaction path for the Diels–Alder reaction of the *s-cis*-1,3-butadiene cation radical with ethene, yielding the cyclohexene cation radical, has been studied at the MP3/6-31G*//3-21G level. The results suggest a concerted, nonsynchronous, activationless cycloaddition in the gas phase.

The development of a diverse and synthetically useful body of cation radical chemistry has been the foremost priority of this research group for more than a decade.[1] The discovery of the aminium salt catalyzed Diels–Alder reaction, reinforced by the subsequent demonstration of the generality and synthetic utility of cation radical Diels–Alder reactions, asserted the relevance of cation radical pericyclic chemistry, and of the associated concept of hole catalysis, to organic synthesis.[2,3] Further implementation

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[1] Bellville, D. J.; Wirth, D. D.; Bauld, N. L. *J. Am. Chem. Soc.* **1981**, *103*, 718–720.

[2] Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1982**, *104*, 2665–2667. Since butadiene is more readily ionized than ethene, the [4+1] surface here is an excited state cation radical surface. To study a ground state [4+1] reaction, a dienophile more readily ionized than butadiene is required.

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