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Origin of the Acidity of Enols and Carboxylic Acids

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Abstract: The origin of the acidity of carboxylic acids and enols has been examined via ab initio MO calculations at the MP2/6-31+G** and Becke3LYP/6-31+G** levels as well as with the CBS-4 and CBS-Q model chemistries. The changes in electron populations that occur on ionization were examined in some detail. In the conversion of vinyl alcohol to its alkoxide ion, the σ electrons of the proton are donated to the oxygen. The repulsion between the increased σ density at oxygen and its π electrons leads to transfer of π electron density to the C═C double bond. At the same time, the negative charge at oxygen repels the σ and π electrons of the attached carbon. A part of the negative charge appears at the hydrogens that are in the nodal plane of the π system. With longer chains, σ/π polarization leads to compensating charge shifts so as to minimize the differences between adjacent carbons. When a carbonyl group is attached, as in carboxylic acids and enols, it serves to stabilize the system by accepting some π electron density (∼0.1 e) and by a stabilizing electrostatic interaction between the positively charged carbonyl carbon and the adjacent negatively charged atom. The stabilization is on the order of 40 kcal/mol for carboxylic acids and 28 kcal/mol for enols. The effect of polar solvents on relative acidities also was examined using a new reaction field model, and experimental observations were reproduced.

1. Introduction

The seemingly simple problem of explaining the greater acidity of formic acid as compared to methanol has generated much recent discussion. In his classic text, *Resonance in Organic Chemistry*, Wheland noted two factors that could lead to the difference in acidity.[2] The first was the resonance stabilization of the formate ion, and the second was the electrostatic stabilization of the negative charge in the ion by the positively charged carbonyl carbon. He stated that it was not possible at that time (1955) to estimate the relative importance of electrostatic and resonance contributions.

Since that time, most chemists have adopted the resonance explanation, and it has appeared in most organic chemistry textbooks.[3] It was first challenged by Siggel and Thomas in 1986 based on the lack of change of the core ionization potentials of the oxygens on going from a carboxylic acid to its anion.[4] This suggests that the change in charge density at the oxygens on conversion to the anion is small. The suggestion was confirmed by several theoretical studies of the charge density distribution in these species in which it was again found that there is not much change in charge density at the two oxygens on going from the carboxylic acid to its anion.[5,6] The two oxygens in the acid already have large negative charges because of their high electronegativity as compared to carbon or hydrogen, whereas the electron population at the acidic hydrogen is small. As a result, there is relatively little charge to be distributed on going to the anion.

Further evidence comes from studies of the potential energy and reorganization energy components of the change in energy on going from a carboxylic acid to its anion, where it was found that the latter term (which would include the resonance stabilization) is quite small.[7] The acidity of a carboxylic acid may then reasonably be related to the positive charge at the carbonyl carbon of the acid that helps to stabilize the carboxylate ion.

Additional evidence may be found in an examination of the acidity of orthoformic acid.[8] We have found that a doubly bonded oxygen has essentially the same effect on the charge at carbon as two single bonds to oxygen.[9] Then, the ionization of orthoformic acid would be comparable to formic acid as far as the charge at carbon is concerned. A calculation of the gas phase acidity of orthoformic acid at the G2 theoretical level gave 352.6 kcal/mol, compared to 381.4 kcal/mol for methanol and 345.7 kcal/mol for formic acid. Thus, 80% of the increased acidity of formic acid may be attributed to the charge at the carbonyl carbon.

However, this viewpoint has not been universally accepted. Dewar and Krull[10] studied the acidity of a series of vinylogs of formic acid using the semiempirical AM1 model and found that the acidity increases as the number of double bonds increases, whereas if the above explanation were correct they had expected that the stabilizing effect of the charge at the carbonyl carbon would decrease with increasing number of double bonds. Exner has raised similar objections to the above viewpoint.[11] A valence-bond study of formic acid by Hiberty and Byrman led to the conclusion that delocalization and inductive effects have equal importance in the stabilization of the anion.[12]

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[2] Wheland, G. W. *Resonance in Organic Chemistry*; Wiley: New York, 1955; p 345.

[3] Cf. Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; p 6. Streitwieser, A.; Heathcock, C. H.; Kosower, E. M. *Introduction to Organic Chemistry*, 4th ed.; Macmillan: New York, 1992; p 486. Ege, S. *Organic Chemistry*, 2nd ed.; Heath: Lexington, MA, 1989; p 95.

[4] Siggel, M. R. F.; Thomas, T. D. *J. Am. Chem. Soc.* **1986**, *108*, 4360.

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[9] Wiberg, K. B.; Hadad, C. M.; Rablen, P. R. To be submitted for publication.

[10] Dewar, M. J. S.; Krull, K. L. *J. Chem. Soc., Chem. Commun.* **1990**, 333.

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Recently, Bordwell and Satish noted that the pK_a of benzoic acid, 1,3-cyclohexanedione (enol), and tropolone are the same in dimethyl sulfoxide.[13] They concluded that the acidity data are not in accord with the theory that the polarity of the carbonyl group is the dominant factor in making the CO_2H function acidic.

In order to clarify the origins of the acidity of the carboxylic acids and the enols, we have carried out ab initio MO calculations that will give better estimates of the relative acidities, and we have analyzed the charge density distributions in order to see what happens to the distribution on going from the acids to their anions. Previous work was carried out using relative small basis sets;[5] the present work makes use of a considerably higher theoretical level. In addition, we have examined the effect of polar solvents on the ionization energies.

2. Structures and Energies

It is known that correction for electron correlation is needed in order to calculate acidities that agree with the gas-phase experimental data, and that diffuse functions are needed in order to properly represent lone pairs. In addition, polarization functions are often needed at hydrogens so that the proton that is lost is properly represented. Therefore, geometry optimizations were carried out using the MP2/6-31+G** and B3LYP/6-31+G** theoretical levels.[14] The latter is a density functional theory model that uses a three-parameter functional that is a hybrid of exact (Hartree–Fock) exchange terms and gradient-corrected exchange and correlation terms, similar to those first suggested by Becke.[15] Both methods were used with the smaller compounds, but only the more computationally economical B3LYP level was used with some of the larger molecules. In each case, the zero-point energy was estimated at the HF/6-31G* level, scaling the calculated frequencies by 0.893.[16] The calculated total energies and zero-point energies are available as supporting information.

Carboxylic acids may adopt either the **Z** or **E** conformations, and both were studied for formic acid (**1**) and benzoic acid (**2**). As has previously been observed,[17] the **Z** conformers with the lower dipole moments were found to have the lower energies. The **E** conformer of benzoic acid was found to have the acid group twisted by 25° with respect to the benzene ring in order to minimize repulsion between the acid proton and the *ortho*-hydrogen on the ring. There are a number of possible conformers of malonaldehyde, its enol (**3**), and its enolate ion. The structures that have been examined are summarized in Figure 1. All three planar conformers of malonaldehyde were found to be transition states, and the minimum energy geometry has a twisted conformation.

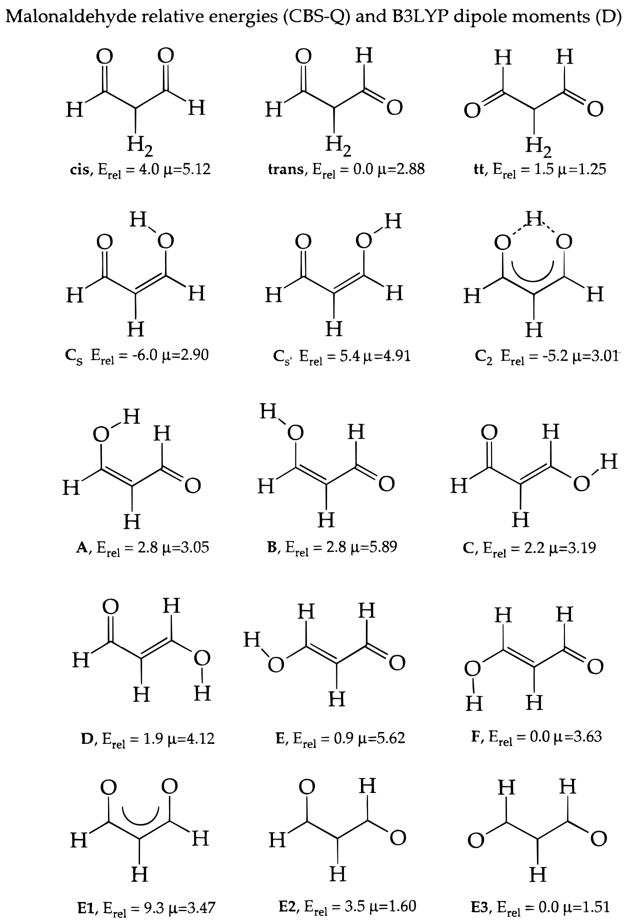

Figure 1. Relative energies of malonaldehyde, its enols, and its enolate ions calculated at the CBS-Q level. The dipole moments are from B3LYP/6-31+G** calculations.

It was not appropriate to use the hydrogen bonded form of **3** in comparing it with the other compounds. With the non-hydrogen bonded enols, conformers ***E*** and **F** have the lower energy and also lead to the lowest energy enolate ion having the two oxygens as far from each other as possible. The corresponding conformers of 5-hydroxypentadienal (**4**), 7-hydroxyheptatrienal (**5**), 1,3-cyclohexanedione enol (**6**), and tropolone (**7**) were examined (Figure 2). The **F** conformers were found to have the smaller dipole moments and the lower energies in each case.

The structures of some of the enols and their enolate ions are summarized in Figure 3.[18] The changes in structure on ionization are fairly constant. In the case of formic acid, the two C–O bond lengths change significantly on ionization, but the relative positions of the hydrogen and two oxygens are hardly changed.[19] The main structural change on ionization is a movement of the carbonyl carbon into a position equidistant from the two oxygens.

In the present study it was important to have reasonably accurate information about the acidities of the acids and enols. Gas-phase acidities are available for only a few of the compounds. Therefore, it was necessary to compute the gas-phase acidities. The use of model chemistries, such as Pople's G2 model,[16] for estimating energies has proven to be remarkably effective in reproducing experimental observations. It is, however, not practical to examine the relatively large compounds in this study using this theoretical model. Therefore, we made use of two recently developed model chemistries, CBS-4 and CBS-Q.[20] The former is applicable to all of the compounds in this study, and the latter was used with the smaller systems.

The CBS-4 model starts with a 3–21G* geometry optimization, then uses a large basis set HF calculation (6-311+G-

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[17] Hocking, W. H. *Z. Naturforsch.* **1976**, *31A*, 1113. Bjarnov, E.; Hocking, W. H. *Z. Naturforsch.* **1978**, *33A*, 610.

[18] The full structural data are available as supporting information.

[19] In formic acid (B3LYP/6-31+G**) the H⋯O distances are 2.01 and 2.05 Å and the O⋯O distance is 2.27 Å. In formate ion, the corresponding distances are H⋯O = 2.02 Å and O⋯O = 2.28 Å. In the acid the two C–O bond lengths are 1.207 and 1.348 Å whereas in the ion both are 1.259 Å.

[20] Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A., Jr. *J. Chem. Phys.* **1996**, *104*, 2598.

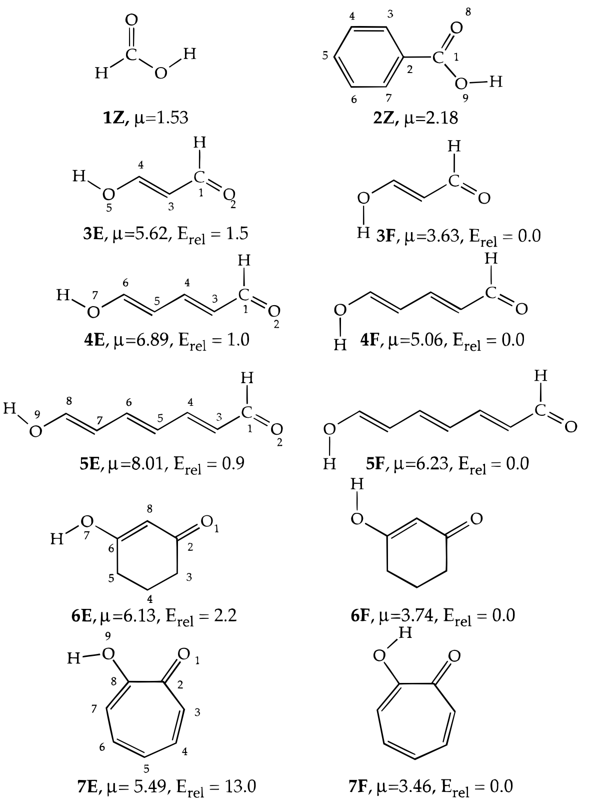

Figure 2. Conformations of acids and enols. The relative energies and dipole moments are derived from B3LYP/6-31+G** calculations. The dipole moments of the **E** conformers of formic and benzoic acids are 4.16 and 5.14 D, respectively. The atom numbering corresponds to that in Table 3.

(2df,p)). The complete basis set (CBS) extrapolation[21] is applied to an MP2/6-31+G†† calculation where the † symbol indicates that the polarization functions have been taken from the 6-311G** basis set. An MP4(SDQ)/6-31G calculation is used to approximate higher than second order effects, and correction is made for the zero-point energy and a size-consistent higher order correction. The CBS-Q model uses a larger basis set at every level of theory. Equilibrium geometries are calculated at the MP2(fc)/6-31G† level, while the CBS extrapolation is based on an MP2/6-311++G(2df,2p) calculation. Higher order contributions are estimated with two calculations: MP4(SDQ)/6-31+G(d,f) and QCISD(T)/6-31+G†. Again, this model has corrections for zero-point energy and higher order effects. In examining a number of organic compounds, the average error in the estimated heats of formation was 2.0 kcal/mol for CBS-4 and 1.0 kcal/mol for CBS-Q.[22]

There are unfortunately only a few experimental data with which the calculations may be compared. The calculated gas-phase acidities are summarized in Table 1. The CBS-4 and CBS-Q energies are in agreement with the experimental values for formic and benzoic acids.

In another study, we found that the gas phase acidities calculated using the CBS-Q model for 16 weak acids agree with the observed values with only a 1.3 kcal/mol rms deviation.[22] Therefore, in the absence of experimental data, we shall choose the CBS-Q values whenever available. However, this level of theory was not practical for the larger acids. A comparison of the MP2, B3LYP, and CBS-4 acidities with those calculated at the CBS-Q level led to good correlations in each case, and an example is shown in Figure 4.

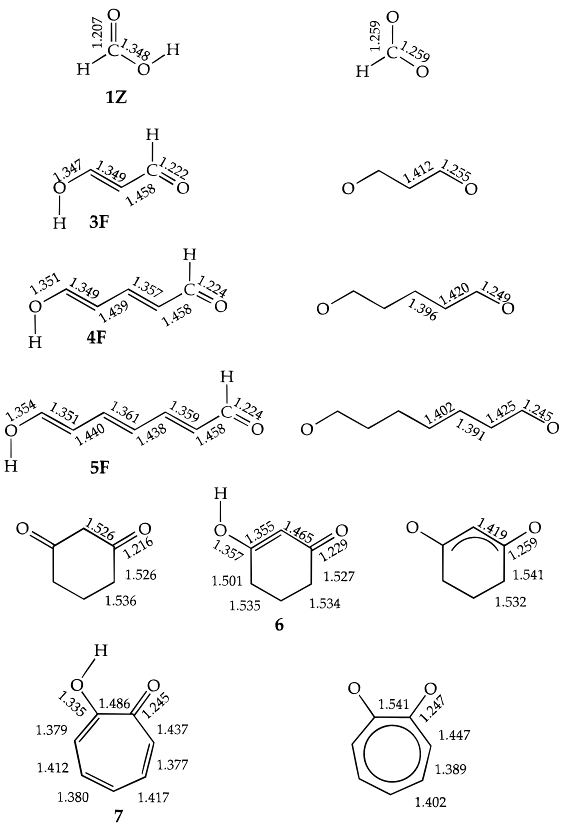

Figure 3. Structures of acids and anions. The bond lengths are derived from the B3LYP/6-31+G** optimizations.

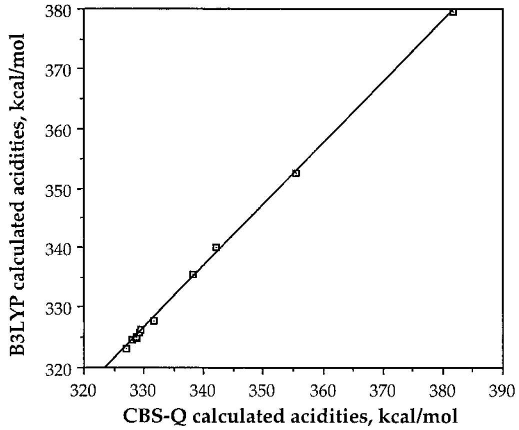

Figure 4. Relationship between the B3LYP and CBS-Q calculated gas-phase acidities.

The remainder of the systems were studied at the B3LYP and CBS-4 levels since they are relatively economical with regard to computer time. The CBS-4 and CBS-Q calculated acidities differ by only a small amount (rms deviation = 0.6 kcal/mol) and therefore the former will be used in the cases where the latter are not available.

The results clearly indicate that malonaldehyde enol (**3F**) is more acidic than formic acid in the gas phase, and that its vinylogs (**4F** and **5F**) have further enhanced acidities. As Dewar has pointed out,[10] the increase in acidity on going from formic acid to malonaldehyde enol is probably due in large measure to moving the two negatively charged oxygens apart, thus

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Table 1. Calculated Gas-Phase Acidities (kcal/mol)

acid	MP2	B3LYP	CBS-4	CBS-Q	obs[a]
formic acid (**1**) (**Z**)	340.9	339.9	341.5	342.2	345 ± 3
formic acid (**1**) (**E**)	336.0	335.5	337.6	338.2	
benzoic acid (**2**) (**Z**)		338.3	339.0		339 ± 3
benzoic acid (**2**) (**E**)		330.8			
malonaldehyde enol (**3**)					
C_s'	329.7	327.7	332.4	331.7	
A	326.8	325.0	329.3	328.7	
B	326.9	324.8	329.5	328.7	
C	327.5	325.8	330.0	329.3	
D	328.0	326.2	330.0	329.6	
E	324.9	323.2	327.3	327.1	
F	326.4	324.7	327.9	328.0	
5-hydroxypentadienal (**4**) (**E**)		317.2			
5-hydroxypentadienal (**4**) (**F**)		318.2	322.2		
7-hydroxyheptatrienal (**5**) (**E**)		313.3			
7-hydroxyheptatrienal (**5**) (**F**)		314.2	319.3		
1,3-cyclohexanedione	334.0	331.0	332.7		
cyclohexanedione enol (**6**) (**E**)	328.3	327.4			
cyclohexanedione enol (**6**) (**F**)	331.3	329.7	330.2		
Tropolone (**7**) (**E**)	326.8	325.5	332.9		
tropolone (**7**) (**Z**)	339.0	338.2	341.9		
methanol	383.2	380.4	380.6	381.8	380.1 ± 0.2
vinyl alcohol	354.4	352.5	355.5	355.4	355 ± 3
1-hydroxybutadiene	342.4	339.7	343.5		

[a] The observed acidities were taken from Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

reducing their repulsive interaction. The smaller changes on going to **4F** and **5F** might also be due to the increased distances between the oxygens.

Whereas malonaldehyde enol was calculated to be more stable than malonaldehyde, in agreement with experimental observations,[23] 3-hydroxycyclohexenone was calculated to have a higher energy than 1,3-cyclohexanedione. Under most conditions, the enol has been found to have the lower energy, but it has been found that in dilute solutions in aprotic solvents the diketone form is preferred,[24] in agreement with the calculations. At higher concentrations the enol becomes favored via the formation of bi- or polymolecular complexes.

The acidities of the cyclohexanedione enols are comparable to that of malonaldehyde enol. In the case of tropolone, the **Z** conformer is stabilized in much the same way as the **Z** conformer of formic acid, and the acidities are about the same as those of the formic acids. The nonstabilized tropolone conformer, **E**, might be the more appropriate form for comparisons with the malonaldehyde enolates, and here again the acidities are comparable. The B3LYP calculated difference in acidity between the **E** and **Z** forms of tropolone (13.0 kcal/mol) seems unusually large, especially since the HF/6-31G* energy difference is only 8.8 kcal/mol. The B3LYP optimization for the **Z** conformer led to an O···H nonbonded distance of 1.80 Å which appears to be unusually short. However, whereas the 6-31G* calculation gave an O···H distance of 1.94 Å, an MP2/6-31+G** calculation gave a distance of 1.82 Å and an energy difference of 12.6 kcal/mol, in good agreement with the B3LYP calculation. The acidities of the tropolone conformers are essentially the same at the MP2 and B3LYP levels of theory, and the CBS-4 calculations give about the same relative energies.

In order to have some additional compounds with which the enols might be compared, the energies of methanol, vinyl alcohol, 1-hydroxybutadiene, and their anions also were obtained. The data are included in Table 1. There is a remarkable increase in acidity on going from methanol to vinyl alcohol, and a further increase on going to 1-hydroxybutadiene. This presumably results in part from the change in hybridization at the carbon bonded to oxygen, but also from the higher polarizability of the double bond and the possibility of distributing some of the negative charge to the carbons in the unsaturated alkoxides.

The increase in acidity on going from methanol to formic acid is 39 kcal/mol whereas the increase from vinyl alcohol to malonaldehyde enol is only 28 kcal/mol. Similarly, the increase in acidity on going from 1-hydroxybutadiene to 5-hydroxypentadienal is 22 kcal/mol.

3. Charge Distributions

Changes in acidity among closely related compounds such as the above must involve changes in charge distributions. We have examined the changes in charge distribution on going from the acids to their anions in two different ways. The first makes use of atomic populations derived from the wave functions, and the second makes a direct comparison of the charge distribution.

Unfortunately, there is no single way in which to derive electron populations at atoms.[25] Although different methods lead to different populations, one might expect that the changes in population on going from an acid to its anion would be similar among different methods. Thus, we made use of the Weinhold−Reed natural population analysis (NPA)[26] and Bader's theory of atoms in molecules (AIM).[27] Both methods agree that the two oxygens bear most of the negative charge in the anions, and both also give large negative charges at oxygen for the parent acids that result from the higher electronegativity of oxygen as compared to carbon and hydrogen. The changes in population on going from the acids to their anions are recorded in Table 2.

In all cases, the two methods agree that the electron population at the acidic proton is only 0.4−0.5 e, corresponding to a

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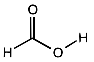
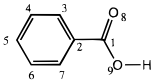
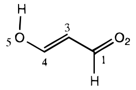
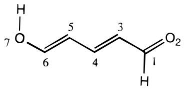
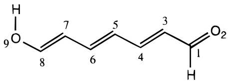
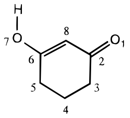
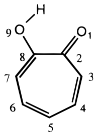
Table 2. Change in Atomic Charges on Going from the Acid to Its Anion

compd	atom	NPA	AIM	atom	NPA	AIM
formic acid (**1**)	C	−0.036	0.072	−O−	−0.080	−0.166
	=O	−0.213	−0.115	H(O)	−0.519	−0.611
	H	−0.152	−0.181			
benzoic acid (**2**)	C1	−0.045	0.177	O9	−0.044	−0.135
	C2	0.058	−0.017	H(C3)	−0.007	−0.015
	C3	−0.041	−0.029	H(C4)	−0.028	−0.049
	C4	−0.025	−0.032	H(C5)	−0.028	−0.052
	C5	−0.060	−0.038	H(C6)	−0.028	−0.048
	C6	−0.024	−0.037	H(C7)	−0.002	−0.007
	C7	−0.032	−0.025	H(O9)	−0.525	−0.614
	O8	−0.169	−0.078			
malonaldehyde enol F (**3**)	C1	−0.064	−0.151	H(C1)	−0.041	−0.068
	O2	−0.166	−0.102	H(C3)	−0.143	−0.055
	C3	−0.105	−0.114	H(C4)	−0.007	−0.138
	C4	0.079	0.347	H(O5)	−0.517	−0.603
	O5	−0.036	−0.117			
5-hydroxypentadienal (**4**)	C1	−0.049	−0.107	H(C1)	−0.032	−0.055
	O2	−0.136	−0.085	H(C3)	−0.025	−0.052
	C3	−0.115	−0.057	H(C4)	−0.027	−0.042
	C4	0.005	−0.029	H(C5)	−0.017	−0.031
	C5	−0.081	−0.092	H(C6)	−0.115	−0.124
	C6	0.105	0.372	H(O7)	−0.514	−0.599
	O7	0.001	−0.099			
7-hydroxyheptatrienal (**5**)	C1	−0.042	−0.090	H(C1)	−0.027	−0.048
	O2	−0.115	−0.073	H(C3)	−0.022	−0.046
	C3	−0.104	−0.046	H(C4)	−0.020	−0.034
	C4	0.008	−0.015	H(C5)	−0.020	−0.036
	C5	−0.099	−0.042	H(C6)	−0.019	−0.034
	C6	0.017	−0.028	H(C7)	−0.029	−0.018
	C7	−0.093	−0.083	H(C8)	−0.088	−0.114
	C8	0.139	0.390	H(O9)	−0.520	−0.598
	O9	0.032	−0.087			
cyclohexanedione enol (**6**)	O1	−0.149	−0.087	H(C3)	−0.033	−0.049
	C2	−0.063	−0.117	H(C3)	−0.029	−0.042
	C3	0.018	−0.001	H(C4)	−0.025	−0.032
	C4	0.000	−0.010	H(C4)	−0.033	−0.054
	C5	−0.003	−0.021	H(C5)	−0.024	−0.035
	C6	0.072	0.399	H(C5)	−0.019	−0.027
	O7	−0.030	−0.121	H(C8)	−0.037	−0.072
	C8	−0.134	−0.130	H(O7)	−0.513	−0.595
tropolone (**7**)	O1	−0.009	−0.060	H(C3)	−0.036	−0.065
	C2	0.002	−0.091	H(C4)	−0.036	−0.061
	C3	−0.105	−0.056	H(C5)	−0.035	−0.067
	C4	−0.029	−0.031	H(C6)	−0.036	−0.059
	C5	−0.108	−0.059	H(C7)	−0.037	−0.017
	C6	−0.036	−0.041	H(O9)	−0.541	−0.592
	C7	−0.088	−0.075			
	C8	0.058	0.367			
	O9	0.038	−0.090			

charge of +0.5 to +0.6. Thus, in the conversion of the acid to its anion, only 0.4−0.5 e must be distributed among the atoms of the anion. In the case of formic acid, both methods agree that the hydrogen attached to the carbonyl group gains about 0.16 e on going to formate ion despite being in the nodal plane of the π electrons. Both of the oxygens in the acids have significant negative charges and on conversion to the anion both oxygens gain some electron density. However the amount of this additional density is relatively small, and much smaller than conventional thinking. There is little change at the carbonyl carbon.

The small change in charge at the carbonyl carbon is of special interest. In the frontier MO (FMO) analysis of a π-conjugative interaction, the π C=O orbital of formic acid would be strongly polarized in the sense $C^{+}-O^{-}$ because of the difference in electronegativity, and therefore the larger coefficient would be at oxygen. Thus, the π* C=O orbital, into which part of the electrons in the lone pair orbital at O^{-} would be donated, would have its larger coefficient at carbon. Then, one would predict that the π-conjugative interaction would lead mainly to an increase in electron density at carbon, rather than at oxygen. This does not agree with the charge distribution that results from the electron populations, and is confirmed by the charge density distribution plots to be described below. The observed charge distribution is $O^{-}-C^{+}-O^{-}$ which leads to maximum electrostatic stabilization. We have found this type of charge distribution to be an important mechanism for stabilization both in saturated compounds[28] and in carbonyl compounds and related derivatives.[29,30]

A similar pattern of charge shifts is found with benzoic acid. Here, the phenyl ring gains some charge density on going to the anion, but again much of it appears at the hydrogens. The somewhat higher gas phase acidity of benzoic acid as compared to formic acid results from the ability to distribute the negative charge over more atoms, including the aromatic protons that are in the nodal plane of the benzene π system. Redistribution

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(28) Wiberg, K. B.; Rablen, P. R. *J. Am. Chem. Soc.* **1993**, *115*, 614.

(29) Wiberg, K. B.; Hadad, C. M.; Rablen, P. R.; Cioslowski, J. *J. Am. Chem. Soc.* **1992**, *114*, 8644.

(30) Wiberg, K. B.; Rablen, P. R. *J. Am. Chem. Soc.* **1995**, *117*, 2201.

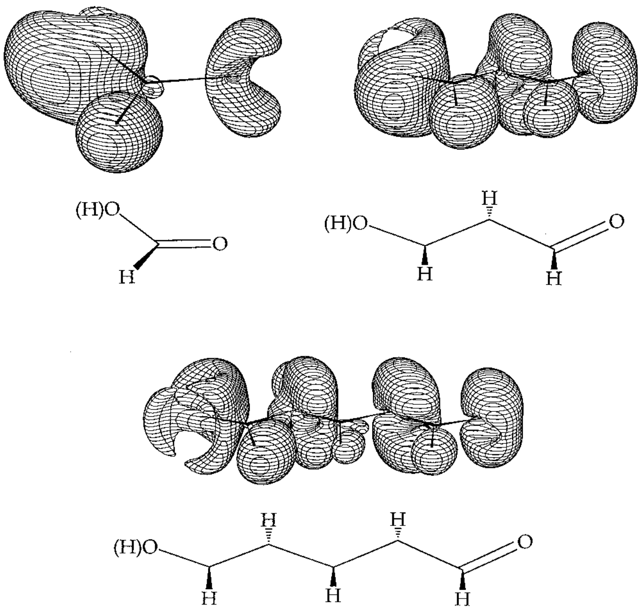


Figure 5. Electron density difference plots for going from the acids to their anions. The compounds are (a) formic acid, (b) malonaldehyde enol **F**, and (c) 5-hydroxypentadienal. The contour level is 0.001 e/au^3, and only the positive contours are shown. Note the increased electron density at the hydrogens that are in the nodal plane of the π-system.

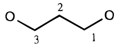
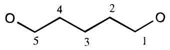
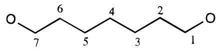
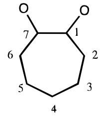
of electrons between σ and π systems is quite common[30] and results from the fact that even though their wave functions are orthogonal, the electrons still repel each other. There is an advantage in placing the charge at the periphery of a molecule since an increase in surface area over which the charge is distributed leads to a decrease in the electrostatic energy.[31]

With the three linear enols, **3**, **4**, and **5**, there is again a common pattern. Both oxygens have relatively large negative charges in the enols. On conversion to the anion, both oxygens gain some charge density, but again the amount is small, and the negative charge is distributed over most of the atoms including the carbon-bound hydrogens that are in the nodal plane of the π-system. The carbon attached to the hydroxy group loses charge density on going to the anion. In the anion, the carbon is next to a negatively charged oxygen that repels the electrons at this carbon. This is the expected effect of classical polarization. The increase in acidity in the series clearly results in part by moving the oxygens farther from each other, in part by having more atoms over which the negative change may be distributed**,** and in part by the greater polarizability of a more extended conjugated system.

The changes in atomic charges are about the same for cyclohexanedione enol (**6**) as for malonaldehyde enol (**3**), which is expected since they are structurally quite similar. It is somewhat less acidic than **3**, which is the expected result of alkyl substitution. Tropolone (**7**) is unique among these compounds in having little change in charge at either oxygen. The ring carbons that would be expected to gain negative charge via a π interaction all gain about 0.1 e, and all of the ring hydrogens gain significant negative charge.

The conclusions concerning the charge distributions in the anions may be checked via the use of density difference maps. Here, it is necessary to use the same geometry for both the acid and its anion so that the effects near the nuclei will cancel. The average geometries were used. 3-D arrays of charge density were calculated for the acids and their anions, and the former was subtracted from the latter. Contour plots showing where the negative charge has gone in forming the anions are shown in Figure 5.

Table 3. AIM Valence Electron Populations for Enolates

enolate	atom	π	σ	total
malonenolate (**E3**, Figure 1)	C1(C3)	0.697	2.403	3.100
	C2	1.171	2.947	4.118
	O(C1,C3)	1.673	5.579	7.252
	H(C1,C3)	0.025	1.051	1.076
	H(C2)	0.039	0.987	1.025
	total	6.000	21.999	27.999
5-hydroxypentadienal enolate	C1(C5)	0.686	2.391	3.076
	C2(C4)	1.131	2.941	4.072
	C3	0.917	3.116	4.033
	O(C1,C5)	1.650	5.583	9.233
	H(C1,C5)	0.024	1.040	1.064
	H(C2,C4)	0.037	0.988	1.025
	H(C3)	0.029	1.002	1.031
	total	8.002	30.002	42.004
7-hydroxyheptatrienal enolate	C1(C7)	0.676	2.387	3.063
	C2(C6)	1.109	2.959	4.068
	C3(C5)	0.926	3.087	4.013
	C4	1.102	2.930	4.032
	O(C1,C7)	1.633	5.587	7.220
	H(C1,C7)	0.023	1.037	1.060
	H(C2,C6)	0.035	0.982	1.017
	H(C3,C5)	0.029	0.998	1.027
	H(C4)	0.036	0.995	1.031
	total	9.999	37.999	47.999
tropolone enolate	C1(C7)	0.697	2.392	3.089
	C2(C6)	1.069	3.006	4.075
	C3(C5)	0.972	3.046	4.018
	C4	1.105	2.941	4.046
	O(C1,7)	1.617	5.581	7.198
	H(C2,6)	0.037	0.985	1.022
	H(C3,5)	0.034	1.011	1.045
	H(C4)	0.044	1.012	1.056
	total	10.001	35.995	45.996

The increased charge density at the hydrogens is easily seen, and confirms the conclusion derived from the changes in atomic charges. The negative charge is distributed everywhere, especially forming the π bonds at the C$-$C single bonds of the enols. Only a small amount of negative charge (~0.1 e) is transferred to the oxygen of the acid carbonyl groups.

In order to confirm the changes in charge at the carbonyl oxygen on going from the acid or enol to the anion that were calculated using the NPA and AIM populations, the charge at these oxygens in Figure 5 was integrated.[32] With formic acid and malonaldehyde enol the increase in charge on going to the anion is 0.15 e and with 3-hydroxypentadienal it is 0.11 e. The values are in good accord with those derived from the populations.

The question of the distribution of σ and π electrons at the atoms of the linear enolates is also of interest. They were obtained using the atoms in molecules procedure, and for a given atom, both the σ and π populations were obtained using the same volume element. The data are shown in Table 3.

The values for 7-hydroxyheptatrienal enolate are of special interest. The traditional resonance formulation predicts that extra π populations would be found at C2, C4, and C6. They are indeed somewhat higher for these carbons, but at the same time, the σ populations are reduced. On the other hand, C5 with a reduced π population has an enhanced σ population. This results in relatively constant total electron populations for these

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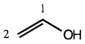
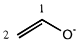
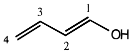
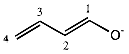
[31] Cf.: Wiberg, K. B.; Schleyer, P. v. R.; Streitwieser, A. *Can J. Chem.* **1996**, *74*, 892.

[32] The value derived by integration depends on the contour value used to define the region of the charge. The value was calculated at a series of increasing contour values starting with 0.005 e/bohr^3 until there was a sharp increase in the value indicating that regions from two atoms began to merge. The values were extrapolated to a zero contour value using a cubic function

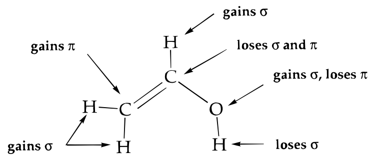
Table 4. AIM Valence Electron Populations for Vinyl Alcohol, 1-Hydroxybutadiene, and Their Anions

compd	atom	π	σ	total
vinyl alcohol	O	1.920	5.220	7.140
	C1	0.910	2.574	3.484
	C2	1.063	2.961	4.024
	H(C1)	0.025	0.933	0.958
	H(C2)	0.034	0.968	1.002
	H(C2)	0.035	0.944	0.979
	H(O)	0.011	0.401	0.412
	total	3.998	14.001	17.999
vinyloxy anion	O	1.757	5.539	7.296
	C1	0.772	2.387	3.159
	C2	1.320	2.944	4.264
	H(C1)	0.031	1.086	1.117
	H(C2)	0.058	1.015	1.073
	H(C2)	0.062	1.029	1.091
	total	4.000	14.000	18.000
1-hydroxybutadiene	O	1.915	5.221	7.136
	C1	0.916	2.568	3.484
	C2	1.050	2.936	3.986
	C3	0.961	3.026	3.987
	C4	0.991	3.043	4.034
	H(C1)	0.025	0.932	0.957
	H(C2)	0.031	0.977	1.008
	H(C3)	0.028	0.974	1.002
	H(C4)	0.032	0.971	1.003
	H(C4)	0.034	0.960	0.994
	H(O)	0.011	0.398	0.409
	total	5.994	22.006	28.000
1-oxybutadiene anion	O	1.706	5.561	7.267
	C1	0.739	2.391	3.130
	C2	1.187	2.915	4.102
	C3	0.949	3.068	4.017
	C4	1.213	2.951	4.164
	H(C1)	0.027	1.065	1.092
	H(C2)	0.041	1.008	1.049
	H(C3)	0.032	1.021	1.053
	H(C4)	0.050	1.011	1.061
	H(C4)	0.055	1.015	1.070
	total	5.999	22.006	28.005

carbons and C5. This effect is due to σ/π polarization, where an increase in π population will repel σ electrons. Such polarization has been found in the rotation about the C$-$N bond in amides and thioamides, and in rotation about the C$-$X bonds in vinyl alcohol and vinylamine.[28]

Similar changes in population are found with tropolone anion. Among the carbons bonded to hydrogens, C4 has the largest π population, but it also has the smallest σ population. Again, the σ/π polarization operates to minimize the differences in total electron population at a carbon.

The changes in electron population on going from vinyl alcohol and 1-hydroxybutadiene to their anions also were examined, and were divided into σ and π contributions (Table 4). The changes for vinyl alcohol may be summarized as follows:[33]



These changes follow in a logical pattern starting with the oxygen. The proton that is lost has only σ density which is transferred to the oxygen. The repulsion between the increased oxygen σ density and its π electrons leads to a donation of π density to the π* orbital of the double bond, a loss of π density at the oxygen, and a gain in π density at the terminal carbon. This effect can also be described classically in terms of the greater polarizability of π-bonds; the π-electrons of the double bond are polarized by the increased charge on oxygen to make one end more positive and the other more negative. The hydrogens at the terminal carbon gain σ density, again via σ/π polarization at the carbon. Similar changes are found with 1-hydroxybutadiene, and again the largest carbon charge is found at the terminal carbon.

The finding that the terminal carbons of these vinylic alcohols gain considerable π density when they are converted to their alkoxide ions provides an explanation of the role of the carbonyl groups in the dione enols, **3**, **4**, and **5**. The C=O group accepts 0.1$-$0.14 e from the terminal carbon of the vinylic alkoxide group, placing this charge density at the oxygen. The carbonyl carbon also helps stabilize the remaining charge at this carbon. These two factors account for the increase in acidity on going from the vinylic alcohols to the corresponding dione enols. The increase in acidity is less than that found on going from saturated alcohols to carboxylic acids, for here the carbonyl group is directly attached to the oxygen that gains the negative charge, leading to a larger energetic stabilization.

4. Solvent Effects

Acidities of organic compounds change markedly on going from the gas phase to solution. This results from two factors. First, in solution, ionization always involves proton transfer to some base, and the proton with its high electrostatic energy is not formed. Second, ions are stabilized by solvents and the degree of stabilization is determined by the size and charge distribution in the ion. Localized charges are strongly stabilized whereas when the charge is spread out, stabilization is reduced. We were interested in exploring these factors for the present group of compounds. Therefore, we have examined the gas-phase reaction of the acids with water to give the anion plus hydronium ion. Since the latter ion also has a high electrostatic energy because of its small size, the reaction of the acid with two water molecules to give the anion plus the hydrated hydronium ion also was studied.

The effect of going to a polar aprotic solvent such as dimethyl sulfoxide was examined using a new version[34] of the polarized continuum model developed by Tomasi et al.[35] Here, the solvent cavity is defined by the 0.0004 e/au^3 surface of the solute, which gives molar volumes in good agreement with the experimental values. The charges on the surface of the cavity are calculated, and their interaction with the solvent, taken as a dielectric continuum, is obtained. The calculated energies are given in Table 5 and the ionization energies are given in Table 6. The solvent effects were calculated at the B3LYP/6-31+G* level since this is far more efficient that using MP2/6-31+G*, and they were obtained using a dielectric constant of 40. The results should be taken as indicating trends that might be expected. A direct comparison with acidities measured in DMSO solution would require a correction for the use of water as the base in the present calculations and DMSO as the base in the experimental studies.[36]

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(33) A similar analysis may be found in ref 5.

(34) Foresman, J.; Keith, T. A.; Wiberg, K. B.; Snoonian, J.; Frisch, M. J. *J. Phys. Chem.* Submitted for publication. Keith, T. A.; Foresman, J.; Wiberg, K. B.; Frisch, M. J. To be submitted for publication. Cf.: Wiberg, K. B.; Rablen, P. R.; Rush, D. J.; Keith, T. A. *J. Am. Chem. Soc.* **1995**, *117*, 4261. Wiberg, K. B.; Keith, T. A.; Frisch, M. J.; Murcko, M. *J. Phys. Chem.* **1995**, *99*, 9072.

(35) Miertus, S.; Scocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117. Tomasi, J.; Bonaccorsi, R.; Cammi, R.; Valle, F. O. *J. Mol. Struct.* **1991**, *234*, 401. Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027.

(36) The relative acidities in DMSO have been successfully correlated with the gas phase acidities using this reaction field model: Wiberg, K. B.; Castejon, H.; Keith, T. A. *J. Comput. Chem.* **1996**, *17*, 185.

Table 5. Calculated Energies, B3LYP/6-31+G**, in $\epsilon = 40$

compd	energy[a]	compd	energy[a]
water	−76.44255	5-hydroxypentadienal (**F**)	−344.58750
hydronium ion	−76.84970	5-hydroxypentadienal anion	−344.11721
$H_5O_2^+$	−153.31891	7-hydroxyheptatrienal (**F**)	−422.00065
formic acid (**Z**)	−189.78382	7-hydroxyheptatrienal anion	−421.52975
formic acid (**E**)	−189.78127	cyclohexanedione	−383.93993
formate ion	−189.30872	cyclohexanedione enol (**F**)	−383.93950
benzoic acid (**Z**)	−420.86318	cyclohexanedione, anion	−383.46014
benzoate ion	−420.38048	tropolone (**Z**)	−420.81642
malonenol, **F**	−267.17505	troplone (**E**)	−420.80408
malonenolate, **E3**	−266.70468	tropolone anion	−420.32767

[a] Gas-phase energies (hartrees): H_2O, −76.43405, H_3O^+, −76.70609; $H_5O_2^+$, −153.20157. Zero-point energies (kcal/mol): H_2O, 12.9; H_3O^+, 20.6; $H_5O_2^+$, 34.7.

Table 6. Gas-Phase and Solution Ionization Energies, B3LYP/6-31+G**, in kcal/mol

	$\epsilon = 1$			$\epsilon = 40$	
compd	HA	HA + H_2O	HA + $2H_2O$	HA + H_2O	HA + $2H_2O$
formic acid (**Z**)	339.9	176.9	139.5	42.1	26.6
formic acid (**E**)	335.5	172.5	135.1	40.8	25.3
benzoic acid (**Z**)	338.3	175.3	137.9	47.2	31.7
malonenol (**F**)	324.7	161.6	124.3	39.1	23.5
5-hydroxypentadienal (**F**)	318.1	155.1	117.7	39.2	23.7
7-hydroxyheptatrienal (**F**)	314.2	151.2	113.9	39.5	24.0
1,3-cyclohexanedione	331.0	168.0	130.6	45.8	30.3
cyclohexanone enol (**F**)	329.5	166.5	129.1	44.7	29.7
tropolone (**Z**)	338.2	175.2	137.8	50.2	34.7
tropolone (**E**)	325.5	162.5	125.2	42.8	27.2

Although the ionization energies decrease considerably when the proton is transferred to water, the gas-phase energies are still quite large. However, when placed in a polar medium, there is a marked reduction in the ionization energies. The major effect of the solvent is found with the ions, and the larger anions are less stabilized than their smaller analogs. As a result, malonaldehyde and its two vinylogs are predicted to have essentially the same acidity in a polar solvent. In general, the whole range of acidities is markedly compressed on going from the gas phase to solution.

It may be noted that benzoic acid is somewhat more acidic than formic acid in the gas phase despite the fact that in aqueous medium formic acid has a significantly greater acidity than benzoic acid. The calculations for the effect of medium on acidity do reproduce the greater acidity of formic acid. Here, the small formate ion is more strongly stabilized by a polar solvent than is benzoate ion. The higher gas-phase energy of the **E** conformer of formic acid may be related to its higher dipole moment as compared to the **Z** conformer. The gas-phase energy difference (4 kcal/mol) is calculated to be reduced to 1 kcal/mol in polar solvents. This is similar to that which we previously found for the **E** and **Z** conformers of methyl formate.[37]

Cyclohexanedione presents an interesting case. Whereas the calculations for the gas phase found the dione to be considerably more stable than its enol, the energies for a polar solvent are found to be essentially the same. It is likely that a hydrogen bonding solvent would further stabilize the enol. Cyclohexanedione and benzoic acid are calculated to have similar acidities in solution, in accord with Bordwell's experimental data, whereas the gas-phase acidities differ by 7 kcal/mol. Here, the similarity in solution acidities appears to be due to solvent effects.

In the gas phase, tropolone and benzoic acid are predicted to have similar acidities, but in solution, benzoic acid is predicted to have a greater acidity. This is not in accord with Bordwell's experimental measurements. However, the gas-phase acidity of tropolone does not appear to have been determined, and so it is not possible at this time to locate the origin of the difference.

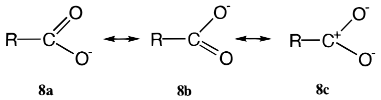
5. Conclusions

The ionizations of enols and carboxylic acids have a number of elements in common. First, the proton lost in the ionization process bears a considerable positive charge, and as a result only about 0.5 electron must be distributed over the anion that is formed. Second, both oxygens in these acids bear considerable negative charge, and both gain some additional negative charge on going to the anion. Third, most of the atoms in the acids and enols gain electron density on going to the anion, and much of it is found on atoms, such as hydrogens, that are in the nodal plane of the π-system.

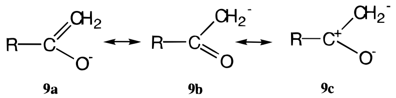
A more detailed examination of the enols makes use of vinyl alcohol as the reference. Here it is found that when the σ electron density associated with the proton is donated to the oxygen on forming the anion, it causes π density at the oxygen to be transferred to the carbon−carbon double bond. In addition, the negative charge at oxygen repels both the σ and π electrons at the adjacent carbon and leads to polarization of the double bond. The combination of these two effects leads to considerable charge transfer to the terminal carbon. The introduction of a carbonyl group at this carbon results in both some charge transfer to the carbonyl group (~0.1 e) and electrostatic stabilization of the negatively charged carbon by the positively charged carbon of the carbonyl group. The net stabilization caused by the carbonyl group is about 28 kcal/mol (i.e. the difference in acidity between vinyl alcohol and malonaldehyde enol).

The conversion of an alcohol to a carboxylic acid by the introduction of a carbonyl group results in the same type of interactions. However, here there is a full negative charge at the oxygen in the carboxylate ion, and the net stabilization increases to about 40 kcal/mol (i.e. the difference in acidity between methanol and formic acid).

These conclusions can also be expressed in conventional resonance structures although the resonance symbolism is limited by its inability to represent σ polarization. The resonance structures **8a** and **8b** for a carboxylate anion express the conventional explanation for the relative acidity of carboxylic acids. The high charge on the oxygens of the carboxylic acid limits the role of these structures relative to the corresponding structures of the carboxylic acid. The polarized structure **8c** is more important than conventionally thought.



Similarly, the stabilization of an enolate ion is conventionally represented only by the structures **9a** and **9b**. Structure **9b** does contribute as shown by the enhanced charge on the terminal carbon of vinylogous compounds but not as much as conventionally thought. Instead, structure **9c** which better represents the polarization of the carbonyl group is clearly much more important than conventionally thought and it is important to consider all three resonance structures. The additional charge shifts that are seen in the σ system also are of importance.



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(37) Wong, M. W.; Wiberg, K. B. *J. Am. Chem. Soc.* **1993**, *115*, 1078.

Our conclusions are in substantial agreement with those of Hiberty and Byrman,[12] except that we find the Coulombic stabilization to be significantly more important than the charge transfer (resonance) stabilization rather than being of equal importance. In addition, we have noted the importance of charge shifts via σ/π polarization to atoms that are in the nodal plane of the π-system. This type of polarization also tends to equalize charges along the carbons of enolate ions.

The calculations also reproduce the change in the relative acidity of formic and benzoic acids on going from the gas phase to solution. They also find that cyclohexanedione has approximately the same acidity as benzoic acid in a polar solvent whereas they differ by 9 kcal/mol in the gas phase. Solvation effects are of considerable importance in determining relative acidities in solution.

6. Calculations

The ab initio calculations were carried out using Gaussian-93.[38] The density difference plots were made using CASGEN.[39] The solvent effects were calculated using the self-consistent isodensity polarizable continuum model (SCIPCM)[34] that has been implemented in the Gaussian code. The NPA charges[26] were calculated using the code implemented in Gaussian-93, and the AIM charges[27] were calculated using PROAIMV, a version of PROAIM that has been modified by Todd Keith.

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Supporting Information Available: Tables of calculated energies, zero-point energies, structural data and electron populations (13 pp). See any current masthead page for ordering and Internet access instructions.

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