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Role of π-Electron Delocalization in the Enhanced Acidity of Carboxylic Acids and Enols Relative to Alcohols

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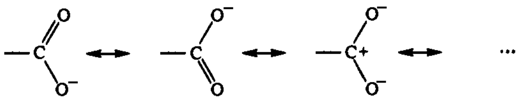
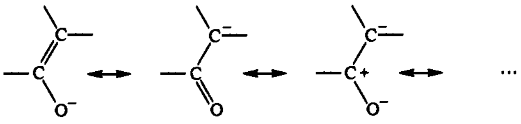
Abstract: The relative importance of π-electron delocalization and induction to the enhanced acidity of carboxylic acids and enols compared to alcohols is examined. These generic classes of molecules are represented by formic acid, vinyl alcohol, and ethanol, respectively. An *ab initio* valence bond method is applied to calculate the energetic effect of π-delocalization in a direct way. The calculations are performed at three different levels of theory. The results are found to be insensitive to the degree of electron correlation. It is concluded that the major geometry changes that the carboxylic acid and enol undergo by loosing their acidic proton are partly—not entirely—explained by π-delocalization. Both inductive effects and π-delocalization are found to contribute, with equal importance, to the acidity of the carboxylic acid. The effect of π-delocalization is predominant in the enol. The recent controversy between the traditional view on the enhanced acidity, entirely based on resonance theory, and a new challenging view, which primarily invokes inductive effects, is discussed.

Introduction

The enhanced acidity of carboxylic acids and enols relative to alcohols has long been attributed to the stabilization of the carboxylate and enolate anions by delocalization of their π electrons (see **1** and **2**); alkoxide anions, as saturated systems, are not subject to resonance stabilization.



1a **1b** **1c**



2a **2b** **2c**

The parent acids and alcohols, on the other hand, are not expected to display any significant mesomeric stabilization because this would involve the participation of some rather unreasonable Lewis structures with separated positive and negative charges. As a consequence, the π-delocalization in **1** and **2** is a factor that lowers the deprotonation energy of carboxylic acids and enols, thus reinforcing their acidity, according to standard organic-chemistry textbooks. However, this traditional view has been challenged by several authors[1-4] on the basis of both experimental and theoretical results and now lies at the center of a lively debate.[1-8] By comparing gas-phase acidities and oxygen core-ionization energies of some organic acids and alcohols, and by considering theoretically calculated net atomic charges, Siggel and Thomas[1] concluded that the acidity difference between carboxylic acids and alcohols is not due to differential effects in the product anions but originates from properties of the undissociated acids and can be explained by electrostatic effects. In response to this point, Exner[5] presented some thermodynamic cycles indicating that the dominant acidifying factor is the stability of the acetate anion, as compared to that of the alkoxide anion. This interpretation has however been questioned by Thomas, Carroll, and Siggel,[2] who argued that the same cycles could be interpreted in terms of an extreme electrostatic model as well.

As an alternative to resonance, the opponents of the traditional view propose the inductive effect of the carbonyl group as the factor responsible for the enhanced acidity of carboxylic acids.[1,3,4] This interpretation is largely based on net atomic charges as calculated within Bader's formalism.[9] According to such computations, the carbonyl group is already highly polar in the carboxylic acid and is not much changed after the acid has lost its acidic proton, so that π-delocalization should be rather minor. From the same kind of population analysis, the enhanced acidity of enols relative to alcohols has been interpreted as arising from the polarity of the vinyl group rather than being due to delocalization of the negative charge in the anion.[4] However, the validity of Bader's electron populations has been questioned by Perrin[6] and Jug and co-workers,[10] who

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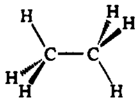
presented arguments suggesting that this formalism may severely exaggerate bond polarities. Other authors have discounted these criticisms.[11]

Another type of argument that has been used, either to support the traditional view or to challenge it, rests on a comparison of theoretical or experimental acidities of series of acids in which the π-electron delocalization and/or the carbonyl inductive effect gradually varies. Streitwieser and co-workers[4] considered the experimental gas-phase acidities (indicated below) of ethane (**3**), formaldehyde (**4**), ethanol (**5**), and formic acid (**6**) and argued that the difference in the acidity of **3** and **4** (29 kcal/mol) is only slightly smaller than that of **5** and **6** (31 kcal/mol). This suggests that resonance in **6** adds little more to the inductive effect of the carbonyl, which operates in **4** as well as in **6**, and should only contribute 2−5 kcal/mol to the enhanced acidity of formic acid. Paradoxically, Dewar *et al.*[7] used another series of (theoretical) acidities, viz. the vinylogues of formic acid (**7**), to demonstrate just the opposite. As the number of CH=CH units increases from zero (formic acid) to three, the inductive effect of the carbonyl on the hydroxyl group vanishes, while delocalization effects are expected to become more important. Since the acidities gradually increase in the series ($n = 0-3$), it was concluded that delocalization, rather than inductive effects, is responsible for the enhanced acidities of formic acid and its vinylogues compared to alcohols. Similar arguments were used to explain the enhanced acidity of enols.



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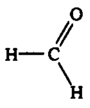
421 kcal/mol



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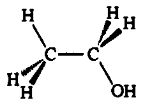
392 kcal/mol



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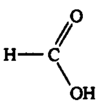
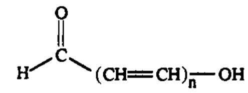
376 kcal/mol



6

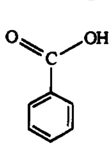
345 kcal/mol



$H-C(=O)-(CH=CH)_n-OH$

7

Very recently, Bordwell *et al.*[8] presented another series of experimental acidities, also as an argument in support of the traditional view. Noting that the acidities in DMSO of benzoic acid (**8**), tropolone (**9**), and 1,3-cyclohexadione (**10**) are nearly identical, while the carbonyl inductive effect is larger in **8** than in **9** and **10**, they concluded that the acidities of these species, which are more acidic than alcohols, must be due to the stabilization of the corresponding anions by delocalization of their negative charge.



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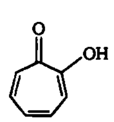

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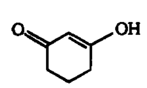

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As convincing as they look to be, arguments based on compared acidities in some sets of molecules may thus lead to contradictory conclusions, depending on which set is chosen. Perhaps the explanation lies in the *a priori* assumptions on which such arguments are based. On the one hand, one might argue that Dewar's and Bordwell's results are not definitely inconsistent with the predominance of the carbonyl inductive effect in carboxylic acids. Indeed, the argument in favor of the traditional view implicitly assumes that there is a significant resonance effect in the carboxylate anion as well as in the other anions of the series, but one could imagine that delocalization is negligible in just that anion and compensated for by a fully efficient inductive effect, which would account for the observed acidities. On the other hand, the series of acidities considered in **3**−**6** by Streitwieser *et al.* are not conclusive either. Their argument rests on the hypothesis that the inductive effect of the carbonyl group is the same in **4** and **6**, which is questionable since the departing hydrogen is directly linked to the carbonyl in **4** but not in **6**.[12] For these reasons and because of the ambiguities attached to a theoretical population analysis, the question of the importance of resonance to the acidities of carboxylic acids and enols is not definitively settled. In fact, what is missing in the experiments and calculations reported up to now is a direct measurement of the stabilization associated with π-electron delocalization.

Ab initio valence bond theory is able to provide such information, owing to its ability to force localization or to allow delocalization of the orbitals at will. It is indeed possible to calculate the energy of a single valence bond structure in which delocalization of the negative charge is turned off and to determine its stability relative to the fully delocalized ground state. Provided that it is used in one of its modern *ab initio* versions with optimized orbitals, valence bond theory has now reached the status of a reliable computational method, yielding compact wave functions with a clearly interpretable content.[13−17] We have thus applied this theory to the problem at hand in order to estimate directly the role of resonance stabilization in the enhanced acidity of carboxylic acids and enols relative to alcohols, these generic molecules being modeled by formic acid, vinyl alcohol, and ethanol, respectively.

Theoretical Methods

The calculations have been performed within the framework of the VBSCF method of van Lenthe and Balint-Kurti,[14] later implemented in an original and very efficient way by Verbeek[15] in the TURTLE[18] program. The method allows for wave functions composed of several valence bond structures, i.e. spin-projected configurations of nonorthogonal orbitals, in which the orbitals are optimized to minimize the total energy. An important feature of the method is that some of the orbitals can be forced to stay localized on an atom or fragment, thus

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(12) One reviewer has pointed out that the acidity difference between **3** and **4** is also due to a change in the hybridization of the acidic carbon atom from sp^3 to sp^2, which leads to an increase in the acidity. Since the acidity of ethylene is about 15 kcal/mol higher than that of ethane, the increase in the acidity from **3** to **4** caused by the inductive effect of the CO group is 15 kcal/mol less.

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allowing the definition of localized diabatic states in which delocalization is turned off. This option will be used to define wave functions representative of localized states which have a π lone pair that is strictly localized on the hydroxyl oxygen atom. On the other hand, letting all orbitals be fully delocalized leads to wave functions of the delocalized ground states, which are equivalent to combinations of all relevant valence bond structures. Note that no localization constraints are imposed on the σ orbitals, which remain fully delocalized in both the localized and delocalized states. So, in spite of their name, the localized states are only localized in part.

The calculations have been performed at three different computational levels, of increasing complexity, devised to introduce π-electron correlation in steps and to treat, within each level, the localized and delocalized states in a balanced way. The three levels, labeled I, II, and III, will be illustrated by the example of the enolate anion (**2**). Note that these refinements are aimed at improving the description of the π-electronic systems, so as to get reliable estimates of the delocalization effects, and are not directed at improving the calculated acidities. More sophisticated methods are required to account properly for the O−H bond dissociation energy and the electron affinity of the dehydrogenated fragment. However, this would lead to wave functions that can no longer be clearly interpreted in terms of localized and delocalized states, while the improvement is of no practical necessity for the problem at hand.

At level I, there is, apart from spin correlation, no electron correlation at all. Both the localized and the delocalized states are described by a single Slater determinant. The delocalized state is calculated by a standard Hartree−Fock method. The localized state is computed in the same way, with the exception that one π orbital is constrained to remain strictly localized on the oxygen atom. The other occupied π orbital may extend over the whole molecule but remains devoid of any oxygen component.

At level II, the delocalized state is calculated by a π-valence-space-CASSCF calculation, i.e. a MCSCF calculation involving all configurations that can possibly be made with an active space of all π valence orbitals and electrons. These valence orbitals include the two π orbitals that are occupied in the Hartree−Fock wavefunction, plus one antibonding virtual orbital. So, the active space involves three π orbitals and four electrons. In the localized state, the π valence orbitals are composed of a pure π atomic orbital on the oxygen atom, which remains doubly occupied, plus one bonding and one antibonding π orbital located between the two carbon centers. Because of the localization constraints, the MCSCF calculation is now reduced to two orbitals and two electrons, which is equivalent to a GVB description of the π bond between the carbon atoms.[19] In both the localized and the delocalized states, level II introduces some left−right electron correlation in the π system.

Level III is aimed at a better description of the negatively charged oxygen in the localized state by taking some radial electron correlation into account. This is accomplished by splitting the doubly occupied π atomic orbital of the oxygen into a pair of singly occupied orbitals that are coupled to a singlet. These orbitals may differ in size and shape but remain strictly localized on the oxygen atom. So, relative to level II, level III brings an additional virtual orbital into play of a nonvalence character. In the delocalized state, this corresponds to a CASSCF calculation involving an active space of four electrons and four orbitals, i.e. the valence space of level II supplemented with the lowest nonvalence π virtual orbital.

The above definitions of localized an delocalized states, illustrated by the example of the enolate anion, are readily extended to the acetate and alkoxide anions, which are also subject to π delocalization, although the corresponding structures for the latter are not as readily drawn as in the two previous cases. In the alkoxide anion, the π system of orbitals is composed of one π atomic orbital on the oxygen atom and two pairs (π_{CH_2} and $\pi^*_{CH_2}$) of pseudo-π fragment orbitals. As previously, a localized state can be defined by locating two π electrons in an atomic orbital that is constrained to remain strictly localized on the oxygen atom. The localized and delocalized states of the parent acids and alcohols are defined similarly. It should be noted that in all cases inductive effects are fully operational, irrespective of the state of localization. Note that the valence bond method above has been applied in its standard form. We did not use our recently developed "breathing orbital" (BOVB) option,[17] which is more accurate but computationally more demanding. Compared to the standard method employed here, the BOVB method brings a further optimization of the delocalized states by defining them as a combination of VB structures that each have their own specific set of orbitals, different from one structure to another. Therefore, the delocalized states calculated in this work can only be slightly disfavored relative to the localized states, so that our calculated delocalization energies represent *lower bounds* of the true delocalization energies.

The calculations were performed with a standard 6-31G* basis set,[20] augmented by p diffuse functions with exponents 0.0438 and 0.0845 for carbon and oxygen, respectively, as recommended for a description of anions.[21] The geometry optimizations of the delocalized states were carried out through a standard gradient technique with the GAUSSIAN92 program.[22] Because no gradient routines were available for the VB calculations, we had to optimize the geometries of the localized states by a rather tedious procedure, viz. an iterative optimization of each geometrical parameter, one by one. All parameters were optimized in this way, except for the C−H bond lengths, which were kept identical to those of the corresponding delocalized ground states.

Results and Discussion

The delocalization energy (DE) of the parent acids and their anions is defined as the energy difference between the localized wave function, ϕ_{loc}, and the delocalized ground state, ϕ_{del}:

$$\mathrm{DE} = E(\phi_{loc}) - E(\phi_{del}) \qquad (1)$$

At this point, it is important to define which geometry is used to calculate the energy of the localized state because different conventions lead to different delocalization energies. One possible choice would be to use the geometry of the delocalized state for the localized state as well. This would lead, by application of eq 1, to the so-called "vertical delocalization energy". However, this quantity is not very useful: it exaggerates the stabilizing effect of delocalization because the optimum geometry of the localized state is expected to be very different from that of the delocalized state. Therefore, a better definition for the DE's refers to the respective optimum geometries of the localized and delocalized states, ϕ_{loc} and ϕ_{del}. Such an energy was recently defined and used by Behrens, Köster, and Jug,[23] and called "adiabatic delocalization energy". This is the definition that will be used in the following to calculate the delocalization energies through eq 1.

Geometries of the Localized and Delocalized States. The geometries of the localized and delocalized states, as optimized at level I, are displayed in Figure 1. Let us first consider the geometries of the localized states, and compare the parent acids with their respective deprotonated anions. In all three cases, it appears that the C−O$^-$ bond in the anion is significantly shorter (respectively 1.324 vs 1.387 Å, 1.353 vs 1.404 Å, and 1.393 vs 1.442 Å) than the corresponding C−OH bond in the parent acid. On the other hand, the adjacent C=O or C=C bond length

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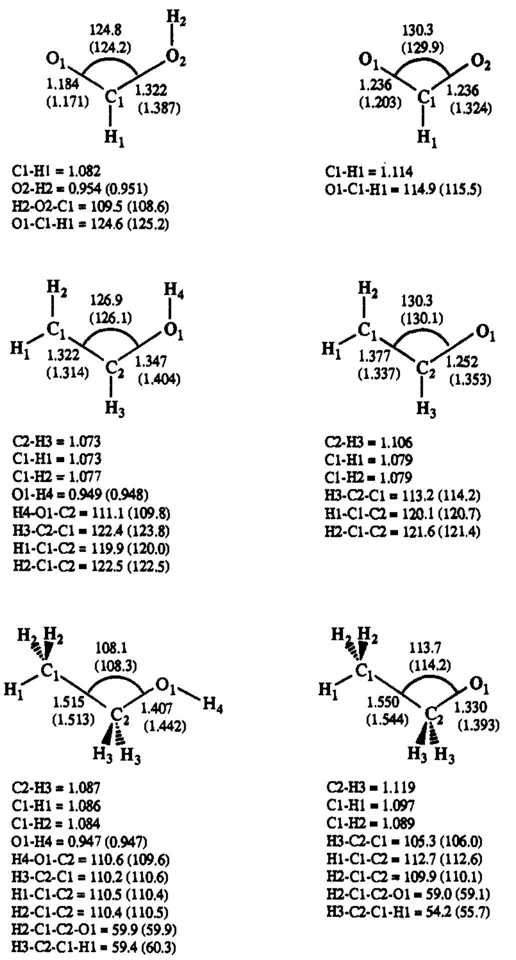


Figure 1. Optimized geometries for the ground states of formic acid, vinyl alcohol, ethanol, and their deprotonated anions. Geometrical parameters for the localized states, in which the delocalization is turned off, are indicated in parentheses.

displays the opposite tendency and increases from the acid to the anion. Such geometry changes just correspond to those expected from an increase of π-electron delocalization. However, this explanation does not hold in the case of localized states, in which π delocalization is totally precluded. This illustrates how fragile are the arguments based on geometry changes alone to make predictions about electronic structures. An alternative explanation can be put forward to account for the tendencies above. The breaking of the O—H bond in the parent acids frees a σ lone pair that then becomes available for hyperconjugation between the hydroxyl oxygen and the central carbon, this all to the detriment of σ hyperconjugation in the adjacent C═C or C═O bond. Thus, the former bond is reinforced and the latter weakened.

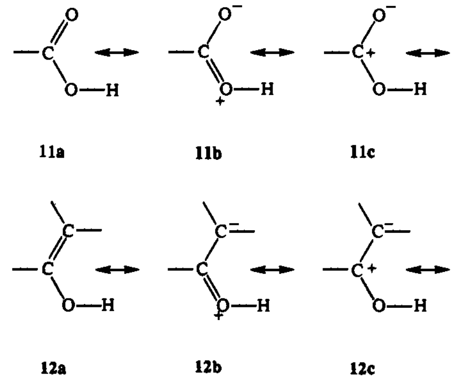
Let us now consider the geometries of the ground states, in which the π-localization constraints are relaxed. With respect to the localized states, the deprotonated anions display an important shortening of the C—O$^-$ bond (respectively 1.236 vs 1.322 Å, 1.252 vs 1.347 Å, and 1.330 vs 1.407 Å) and, to a lesser extent, a lengthening of the C═C or C═O bond, indicative of a significant delocalization effect, which is more important in the carboxylate and enolate anion than in the alkoxide anion. This asymmetry between bond lengthening and bond shortening has nothing surprising and finds a simple rationalization with the example of carboxylate anion. To go from the localized state, which has one double and one single bond, to the delocalized state, which has two equivalent bonds, one has to stretch the double bond and to compress the single σ bond. Since the latter process is the easiest one, it logically plays the major role in the overall geometry change. A similar reasoning applies to the enolate and alkoxide anions.

Remarkably, relaxing the localization constraints significantly affects the geometries of the parent acids, indicating that π conjugation is not at all negligible in these species. Thus, two conclusions can be drawn from our consideration of the optimized geometries displayed in Figure 1: (i) Both the acids and the deprotonated anions are subject to some π-electron delocalization. In accord with chemical intuition, the effect of delocalization is more important in the carboxylate and enolate anions than in the other species. (ii) The geometry changes that the acids undergo under deprotonation are only partly explained by π delocalization.

Delocalization Energies. The absolute energies of the localized and delocalized states are displayed in Table 1. The energetic effect of π-delocalization can be calculated from them through eq 1. In Table 2 the resulting delocalization energies are summarized.

The results at our computational level I show that the carboxylate and enolate anions have the largest delocalization energies among the six species, in accordance with the principles of resonance theory. This is because none of these anions can possibly be described by a single Lewis structure. For example, the carboxylate anion, with its symmetrical geometry, requires besides structure **1a** at least the contribution of **1b**. This also applies to the enolate anion, but with an important difference: **1a,b** are degenerate structures, a factor that is expected to maximize the resonance energy, while the unequivalent structures **2a,b** have different energies. Accordingly, the delocalization energy is expected to be smaller in the enolate anion than in the carboxylate anion, in agreement with the computed values of 34.9 and 40.2 kcal/mol, respectively.

As expected, the parent acids of these two anions have much smaller delocalization energies.[24] Indeed, π delocalization is less favorable in these cases because each of these acids is reasonably well described by a single Lewis structure, viz. **11a** and **12a**. The other conceivable structures require the creation of a pair of charges, as in **11b** and **11c**, or in **12b** and **12c**, and are therefore higher in energy. Also in ethanol and its deprotonated anion, for which no resonance between low-lying Lewis structures may be expected, the delocalization energy is relatively small.



11a **11b** **11c**

12a **12b** **12c**

The calculations have been carried out at higher levels of theory for the carboxylate and enolate anions and their parent acids to investigate the possible effect of π-electron correlation

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[24] Note that the delocalization energies in the parent acids are related to the rotational barriers around the C—OH bonds but are larger than these latter quantities, which are on the order of 5—6 kcal/mol in formic acid and vinyl alcohol. This is because the 90°-rotated conformer also has some π-conjugation in its π or pseudo-π system and has a non-negligible delocalization energy.

Table 1. Absolute Energies (hartrees) of the Deprotonated Anions and Their Parent Acids as Calculated at the Various Computational Levels[a]

	localized states			delocalized states		
	level I	level II	level III	level I	level II	level III
			Anions			
$HCOO^-$	−188.140 710	−188.166 115	−188.179 916	−188.204 758	−188.226 911	−188.244 762
CH_2CHO^-	−152.254 223	−152.276 413	−152.290 016	−152.309 880	−152.331 149	−152.344 303
$CH_3CH_2O^-$	−153.428 798			−153.452 125		
			Acids			
HCOOH	−188.739 168	−188.769 087	−188.780 439	−188.767 107	−188.794 851	−188.807 336
CH_2CHOH	−152.872 742	−152.900 183	−152.911 349	−152.894 345	−152.919 860	−152.931 785
CH_3CH_2OH	−154.069 585			−154.080 030		

[a] The delocalized and localized states correspond to resonance turned on and off, respectively. The corresponding geometries are optimized at level I.

Table 2. Delocalization Energies of the Deprotonated Anions and Their Parent Acids as Calculated by Eq 1 at the Various Computational Levels

	DE (kcal/mol)		
	level I	level II	level III
	Anions		
$HCOO^-$	40.2	38.1	40.7
CH_2CHO^-	34.9	34.3	34.1
$CH_3CH_2O^-$	14.6		
	Acids		
HCOOH	17.5	16.2	16.9
CH_2CHOH	13.6	12.3	12.8
CH_3CH_2OH	6.6		

Table 3. Contributions of the Delocalization Energies to the Acidities of Formic Acid, Vinyl Alcohol, and Ethanol as Calculated by Eq 2 at the Various Computational Levels

	ΔDE (kcal/mol)		
	level I	level II	level III
HCOOH	22.7	21.9	23.8
CH_2CHOH	21.3	22.0	21.3
CH_3CH_2OH	8.0		

on the delocalization energies. Ethanol and the ethoxide anion were excluded from this more extensive study because their pseudo-π systems include contributions from the out-of-plane hydrogen atoms. For these molecules, the following higher levels are less clearly defined than in the truly planar systems. This is, however, of no practical importance because the contribution of delocalization to the acidity of ethanol is very small anyway. We are therefore left with four topologically equivalent π systems, involving four electrons and three centers, so that a comparison of correlation effects can be made in a meaningful way.

The delocalization energies calculated at the levels II and III are displayed in Table 2. The values prove to be practically identical to those calculated at level I, within 2 kcal/mol. This shows that the π-electron correlation energy, albeit quite significant, has about the same magnitude in the localized and delocalized states and has a negligible influence on the effect that is investigated in this study.

Although both the carboxylate and enolate anions are stabilized by sizeable delocalization energies, these quantities do not directly reflect the contribution of delocalization to the acidities because the parent acids are also significantly delocalized. As delocalization reinforces acidity only if it stabilizes the anion more than the parent acid, the contribution of delocalization to the acidity is best defined as the difference of the two delocalization energies:

$$DE = DE(\text{anion}) - DE(\text{acid}) \qquad (2)$$

The ΔDE values, as calculated at the different computational levels, are displayed in Table 3. It appears that delocalization contributes rather little (8 kcal/mol) to the acidity of ethanol, as expected from chemical intuition. In fact, simple qualitative resonance theory would predict no delocalization at all, so that the π delocalization is perhaps better viewed as hyperconjugation instead of resonance between mesomeric formulas. In contrast, delocalization contributes as much as 21−23 kcal/mol to the acidity of formic acid and vinyl alcohol. Perhaps surprisingly, the ΔDE values are the same for the two species, while one might have expected resonance effects to be more important in formic acid, which mesomeric description of its anion involves two equivalent structures, namely **1a,b** (**2a,b** of the enolate anion have unequal weights since oxygen is more electronegative than carbon). The explanation probably lies in the polar nature of the C−O bond, which results in a large contribution of structure **1c** to the anion. Since an ionic structure of the same type is also important in the undissociated acid, the nature of the π electronic system changes less than expected from acid to anion, so that the change in delocalization energy remains relatively moderate. To push this reasoning to the limit: if the C−O bonds were entirely ionic, there would have been no resonance at all.

This does not mean that enols and carboxylic acids have comparable acidities, of course, since inductive effects may also contribute to the acidities. In that respect, it is useful to compare the ΔDE values of Table 3 with the total acidity enhancements of formic acid and vinyl alcohol compared to ethanol. The experimental gas-phase acidities of formic acid and ethanol are known to be 345 and 376 kcal/mol, respectively.[25] The acidity of vinyl alcohol has been accurately calculated by Streitwieser and co-workers,[4] who predicted a value of 359.5 kcal/mol. So, the acidities of formic acid and vinyl alcohol are reinforced by 31 and 16.5 kcal/mol, respectively, relative to ethanol. By comparison, our calculations (level I) indicate that delocalization contributes 23, 21, and 8 kcal/mol, respectively, to the acidities of formic acid, vinyl alcohol, and ethanol. Delocalization therefore reinforces the acidities of the two former species by 15 and 13 kcal/mol, respectively, compared to ethanol, which is 48% and 78% of the total acidity enhancement. It is thus seen that delocalization accounts for the major part of the acidity enhancement in vinyl alcohol and for only half of the enhancement in formic acid. Other effects must therefore be invoked for the other half in this latter molecule, and one may a priori think of two factors: the bond strength of the O−H bond and the electron affinity of the anion. The first factor may be eliminated as the experimental O−H bond strengths of ethanol and formic acid are rather similar, 106.1 and 104.2 kcal/mol,

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(25) Bartmess, J. E.; McIver, R. T., Jr. *Gas Phase Ion Chemistry;* Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, p 87.

respectively.[26] The second factor corresponds to the stabilization of the anion, which is traditionally related to delocalization or induction. It may therefore be attributed, following Siggel, Thomas, and Streitwieser,[1-4] to inductive effects.

Conclusions

In order to separate inductive effects from delocalization effects in the enhanced acidities of carboxylic acids and enols relative to alcohols, and with the aim of quantifying delocalization effects in a rigorous way, we have calculated the π-delocalization energies of formic acid, vinyl alcohol, and ethanol and their deprotonated anions by a direct method, using *ab initio* valence bond theory. These molecules may serve as representatives of the general classes of molecules carboxylic acids, enols, and alcohols.

Compared to those of their parent acids, the geometries of the carboxylate and enolate anions are significantly altered in a way expected from simple resonance theory. However, these geometry changes are only explained in part by an increase of π-electron delocalization.

Delocalization and inductive effects are found to be of equal importance to formic acid: both contribute about 15 kcal/mol to the acidity enhancement of this acid relative to ethanol. The delocalization effect is therefore larger than predicted by Streitwieser and co-workers,[4] who estimated this factor to be 2−5 kcal/mol, which is only 6−16% of the acidity difference. By contrast, delocalization is predominant in vinyl alcohol and is responsible for most of its enhanced acidity relative to ethanol.

It is clear that our calculations support the traditional view by showing that delocalization is an important factor responsible for the enhanced acidity of carboxylic acids and enols relative to alcohols, especially since our calculations provide lower bounds of the delocalization effects, as indicated in the Theoretical Methods. However, Streitwieser's[4] challenging view is also confirmed in part because inductive effects prove to be on the same order of magnitude as delocalization effects in carboxylic acids.

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[26] 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), p 677, 662.