Acidity of Carboxylic Acids: Resonance Delocalization or Induction?

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On the basis of calculated acidities of the vinylogues of formic acid and vinyl alcohol, Dewar and Krull have concluded that the higher acidity of carboxylic acids relative to alcohols is due to stabilization of the conjugate anion by resonance delocalization. More detailed calculations on some of the compounds that they have considered shows indeed that delocalization of charge in the anion plays a role in the acidity of buta-1,3-dien-1-ol **1** relative to vinyl alcohol and of 3-hydroxyprop-2-enal **2** relative to formic acid. However, these calculations show that this conclusion is not applicable to the relative acidities of ethanol, vinyl alcohol and formic acid or of **2** relative to **1**. These are due to the charge distribution in the neutral molecule, in keeping with the ideas proposed by Siggel *et al.*

That carboxylic acids are stronger acids than alcohols is well known. The usual textbook explanation[1,2] for this is that the anion of a carboxylic acid is stabilized by resonance delocalization of the negative charge over the two oxygens of the carboxyl group.† No similar delocalization is possible for alcohols.

This view was challenged by Siggel and co-workers[3,4a] who used experimental measurements of oxygen core-ionization energies and gas-phase acidities to show that differences in delocalization of charge in the anion contribute negligibly to the difference in acidity between carboxylic acids and alcohols, and that this is due to differences in the charge distribution in the neutral molecules. Theoretical calculations of the factors that influence acidity confirm the conclusions that they reached on the basis of experimental data.[3,4a,5]

Siggel, Streitwieser and Thomas,[4] in considering this problem further, showed through several arguments that resonance does not play a major role in the acidity of carboxylic acids relative to that of simple alcohols, but that the greater acidity of carboxylic acids is due primarily to the inductive effect of the carbonyl oxygen. Recent analyses by Taft *et al.*[6] also conclude that the acidities of formic and acetic acids are due primarily to an inductive effect.

The conclusions reached by Siggel and Thomas[3] and by Siggel, Streitwieser and Thomas[4b] have been the subject of criticism. Among these is the work of Dewar and Krull,[7] who concluded from the calculated acidities of the vinylogues of formic acid and vinyl alcohol that these acidities can be explained in terms of resonance stabilization of the conjugate anion. They present these results as a refutation of the view put forth by Siggel *et al.* Here, I present the results of additional calculations on some of the molecules that were considered by Dewar and Krull. These results show that the conclusions reached by them regarding the role of resonance stabilization of the conjugate anion cannot be supported. Before presenting these results, I review the arguments presented by Siggel *et al.* and some of the discussion that has followed.

Background

The term 'acidity' has been used to refer qualitatively to the strength of an acid and quantitatively to either ΔE°, ΔH° or ΔG° for the removal of a proton from the acid. Following the usage of Dewar and Krull, E_d (deprotonation energy) is used to represent $\Delta E_0^\circ = \Delta H_0^\circ$ for the reaction $RH \longrightarrow R^- + H^+$. A small deprotonation energy corresponds to a strong acid.

Using both classical and quantum mechanical arguments, Siggel and Thomas[3] showed that

$$E_d = -V - R \qquad (1)$$

Here V is the potential energy of a unit positive charge at the site of the acidic proton in the neutral molecule; it is negative. V/e is the potential from which the proton must be removed. R represents a relaxation energy arising from the rearrangement of electrons and nuclei accompanying removal of the acidic proton. The energy of the final ionic state and, hence, the deprotonation energy, is lowered by this relaxation, which includes the effects of resonance delocalization as well as other electronic or geometric rearrangement in the anion.

The difference in deprotonation energy, ΔE_d, between two acids, for instance, formic acid and methanol, is shown in eqn. (2).

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

In the traditional view of acidity,[1] the difference between these two acids arises from differential stabilization of the anions by electron rearrangement, with resonance stabilizing the formate ion more than the methoxide ion. Thus ΔV would be expected to be *ca.* 0 and ΔE_d to be approximately equal to $-\Delta R$.

Experimentally, Siggel and Thomas determined ΔV and ΔR from measurements of gas-phase acidities and core-ionization energies. Theoretically, they evaluated these from *ab initio* electronic structure calculations of E_d and V, using eqn. (1) to obtain R. By both methods they found that ΔR is small and that the acidity of carboxylic acids relative to alcohols is determined almost entirely by the potential at the proton, which, in turn, is determined by the charge distribution in the neutral molecule.

It is to be noted that there are two separate considerations here. First, what is the importance of charge delocalization in the anion relative to charge distribution in the neutral molecule in determining the acidity? Second, what is the importance of resonance, in either the anion or the neutral molecule, relative to inductive effects in determining the acidity? The work of Siggel and Thomas addressed the first of these questions and showed that delocalization in the anion (whether due to resonance or other forms of delocalization) plays a negligible role in the acidity of carboxylic acids relative to alcohols.

The second question was addressed by Siggel, Streitwieser

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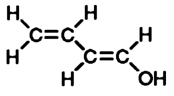
† An exception is Solomon's text, ref. 2, which accounts for the acidity of carboxylic acids in terms of the explanations proposed in refs. 3 and 4.

Table 1 Calculated values of deprotonation energies, E_d, initial-state potential energies, V, and relaxation energies, R

Compound	E_d	V	R/eV
Methanol	17.33	−27.48	10.16
Ethanol	17.23	−27.53	10.30
Vinyl alcohol	16.01	−26.58	10.57
Formic acid	15.47	−25.64	10.16
Buta-1,3-dien-1-ol	15.51	−26.69	11.18
3-Hydroxyprop-2-enal	14.91	−25.72	10.81
	ΔE_d	ΔV	ΔR
Ethanol	0.00	0.00	0.00
Vinyl alcohol	−1.22	0.95	0.27
Formic acid	−1.76	1.89	−0.14
Vinyl alcohol	0.00	0.00	0.00
Formic acid	−0.54	0.95	−0.41
Buta-1,3-dien-1-ol	−0.50	−0.11	0.61
Formic acid	0.00	0.00	0.00
3-Hydroxyprop-2-enal	−0.56	−0.09	0.64
Buta-1,3-dien-1-ol	0.00	0.00	0.00
3-Hydroxyprop-2-enal	−0.59	0.97	−0.38

and Thomas,[4b] and by Taft, Koppel, Topsom and Anvia.[6] Siggel *et al.* used several arguments to show that inductive effects account for most of the acidity of simple carboxylic acids. The analysis by Taft *et al.*[6] shows that the predominant effect on the acidity of formic and acetic acids relative to methanol and ethanol is an inductive effect, although resonance appears to play a significant role.

Dewar and Krull[7] have presented calculations on the deprotonation energies of ethanol, formic acid, vinyl alcohol and the vinylogues of vinyl alcohol (of which buta-1,3-dien-1-ol **1** is an example) and of formic acid (of which 3-hydroxyprop-2-enal **2** is an example). They note that the vinylogues have lower E_ds than the parent compounds, vinyl alcohol and formic acid, and make the reasonable conclusion that the lower values of E_d are due to resonance effects in these conjugated systems. They conclude that these results 'vindicate the traditional explanation for the acidity of formic acid' and 'that the acidity of carboxylic acids is due primarily to resonance stabilization of the conjugate anions'. This logic is faulty. Whereas it may be reasonable to conclude that the lower values of E_d for the vinylogues are due to resonance, this does not imply that the differences between ethanol and formic acid are also due to resonance. Furthermore, the results obtained by Dewar and Krull provide no insight into the question of whether the differences in E_d are due to the initial-state charge distribution or to charge rearrangement in the conjugate anion.



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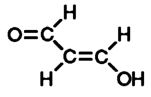

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Here I present the results of additional calculations on some of the molecules considered by Dewar and Krull. These include calculation of the E_ds, initial-stage potential energies, V, and final-state relaxation energies, R. The results for methanol, ethanol and formic acid are in complete agreement with the ideas put forth by Siggel and Thomas. Those for vinyl alcohol and the vinylogues of vinyl alcohol and formic acid illustrate the complexity of these systems.

Calculations

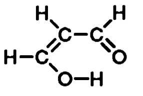
The GAUSSIAN 90 program[8] has been used for electronic structure calculations on methanol, ethanol, vinyl alcohol, formic acid, buta-1,3-dien-1-ol **1** and 3-hydroxyprop-2-enal **2**. The relevant quantities are the total energies for the neutral molecules and appropriate anions and the potential energy, V, of the acidic hydrogen in the neutral molecule. The potential energy of a unit positive charge at some point $\mathbf{r}_0$ in the molecule is determined from the expression shown in eqn. (3), where ρ is the electronic charge density, Z_i is the charge on the ith

$$V(\mathbf{r}_0) = -\int \frac{\rho(\mathbf{r})}{|\mathbf{r}_0 - \mathbf{r}|}\,d\tau + \sum_i \frac{Z_i}{|\mathbf{r}_0 - \mathbf{r}_i|} \tag{3}$$

nucleus located at $\mathbf{r}_i$. (If $\mathbf{r}_0$ refers to the location of one of the nuclei, as it does in this problem, then that nucleus is omitted from the sum.) The charge density, ρ, is determined from the electronic wavefunctions determined in the Hartree–Fock calculation. E_d is equal to the difference between the energy of the anion and that of the neutral molecule. The relaxation energy, R, is obtained from eqn. (1): $R = -E_d - V$.

For each neutral molecule, the conformation was determined by optimizing at the 3-21G level. Once this was determined the geometry was optimized using the 6-311++G** basis set at the Hartree–Fock level. The anions were assumed to have the same conformation as the neutral molecules and were optimized with this conformation also at the HF/6-311++G** level.

3-Hydroxyprop-2-enal is a planar molecule. Its lowest energy conformation has the hydroxy oxygen *cis* to the carbonyl carbon **3**. This is, however, probably not the best conformation for the question at hand because of the possible close interaction between the acidic proton and the carbonyl oxygen. Instead, calculations were done with the *trans* form, of which the lowest energy conformer is **4**. Buta-1,3-dien-1-ol is non-planar; one view of it is **5**. This shows an apparent short distance between the hydroxy hydrogen and the hydrogen at the other end of the chain. However, one of these is below the average plane of the molecule and the other is above. As a result, the distance between them is 2.3 Å. The other molecules have conformations that have been previously discussed.[4b,9]



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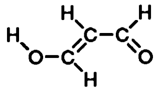

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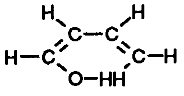

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The results of these calculations are summarized in Table 1. The upper part of the table shows the calculated values of E_d, V and R. The column R is based on calculations for the optimized anion and includes both electronic and geometric relaxation. The lower part of the Table shows some of these quantities relative to those for ethanol (first group), vinyl alcohol (second group), formic acid (third) and buta-1,3-dien-1-ol (fourth). The values reported here differ slightly from those calculated by Dewar and Krull, but the essential features are the same.

Discussion

Ethanol–Formic Acid.—From Table 1 we see that ΔV for formic acid relative to ethanol is −1.76 eV, whereas ΔR is −0.14 eV. These results are in complete accord with those calculated for similar molecules by Siggel and Thomas,[4] using lower-level calculations, and by Ji and Thomas[5] using higher-level calculations. As has been pointed out before, the essential difference between the acidity of these two compounds arises from the initial-stage charge distribution. The contribution from delocalization of charge and geometric relaxation in the anion is small, and overall, is in the opposite direction from that expected from the traditional view of resonance delocalization, which would have predicted a positive sign for ΔR.

Ethanol–Vinyl Alcohol.—The results for vinyl alcohol show that it is a stronger acid than ethanol and that the principal reason for the lower deprotonation energy is, as is the case for formic acid, in the value of ΔV, which comes from the initial-state charge distribution. This result can arise because of resonance forms such as

which remove negative charge from the vicinity of the acidic proton and because the sp^2 carbon in vinyl alcohol has a higher electronegativity than the sp^3 carbon in ethanol.

This result is completely consistent with our experimental and theoretical studies of ethyl and vinyl halides, where we have found that the vinyl group creates a more positive potential at the halogen than does the ethyl group.[10] The same phenomenon can be seen in the dipole moments of vinyl chloride (1.45 D) and ethyl chloride (2.06 D). The lower dipole moment for vinyl chloride can be understood as arising from donation of negative charge from the chlorine to the vinyl group *via* structures similar to those shown above for vinyl alcohol and from the higher electronegativity of the sp^2 carbon.

The Vinylogues.—The last three groups of entries in Table 1 show the results for the vinylogues relative to the parent compound and relative to each other. We see that the two vinylogues are both more acidic than their parent compounds by about 0.5 eV. Moreover, this higher acidity (lower E_d) is due entirely to relaxation in the final state. The potential-energy shifts are small and favour an acidity shift in the opposite direction. For the most part, these results are entirely consistent with the ideas put forth by Dewar and Krull and point to an important role for delocalization of charge in the anion in determining the acidity of these compounds. This result cannot, however, be extended to the difference in acidity between alcohols and carboxylic acids, as the results discussed above indicate.

The last two lines of Table 1 show a comparison of the two vinylogues. Not surprisingly, the one with a carbonyl oxygen is more acidic than the one without. Significant, however, is the observation noted by Dewar and Krull that the change in deprotonation energy between buta-1,3-dien-1-ol and 3-hydroxyprop-2-enal (-0.59 eV) is almost identical to that between the parent compounds, vinyl alcohol and formic acid (-0.54 eV). If the acidity of these compounds is governed solely by an inductive effect, then we would expect that the influence of the terminal carbonyl oxygen would fall off with the length of the chain. Dewar and Krull note that the observed result is consistent with resonance stabilization in the conjugate anion.

Further inspection of the last two lines of Table 1 and the line comparing formic acid with vinyl alcohol shows, however, that the important contribution to these acidity differences is in ΔV (about 0.95). The contribution from ΔR for both pairs is negative, indicating that delocalization in the anion favours higher acidity in the compound without the carbonyl oxygen and is opposite to the trend observed in the calculated acidities. It is striking that ΔV is nearly the same for both pairs, indicating that the effect of the oxygen is efficiently transmitted through the conjugated chain. This result points to a role for resonance in determining the acidity of these compounds, but it is resonance in the neutral molecule and not in the anion.

Conclusions

The more detailed analysis presented here of the compounds considered by Dewar and Krull leads to the following conclusions. (*i*) Resonance delocalization in the anion does not contribute to the difference in acidity between ethanol, vinyl alcohol and formic acid. The difference is due to the initial-state charge distribution. This result is in agreement with the view presented by Siggel and Thomas. (*ii*) Resonance effects may contribute to the acidities of **1** and **2**, as suggested by Dewar and Krull. (*iii*) Considering these two compounds relative to their parent compounds, vinyl alcohol and formic acid, we see that the acidity difference arises from differential stabilization of the conjugate anions, in agreement with the conclusions of Dewar and Krull. (*iv*) Considering **2** relative to **1**, the acidity difference arises from differences in the charge distribution in the neutral molecule. This may be interpreted as showing the efficiency with which the conjugated system can transmit the electron-withdrawing effect of the carbonyl oxygen from one end of the molecule to the other.

Only when we consider **1** and **2** relative to their parent compounds do we see a role for resonance stabilization of the anion in determining acidity differences. We cannot, however, from this result make a categorical statement that resonance delocalization plays a role in determining other acidities. In almost all other cases, not only those presented here, but those discussed elsewhere, the principal factor that determines acidity is the charge distribution in the neutral molecule and the potential at the acidic proton that is produced by this charge distribution.*

It is to be noted that calculations of the sort presented here provide information only on the importance of the initial-stage charge distribution *vs.* that of final-state charge rearrangement. They do not, by themselves, shed any light on whether the initial-stage charge distribution is governed predominantly by inductive effects or predominantly by resonance effects. We need to draw on other kinds of chemical information, such as that presented by Siggel *et al.*[4b] and Taft *et al.*[6] to answer this question. The combined evidence points toward an inductive effect on the initial-stage charge distribution as being the most important contributor to the acidity of formic and acetic acid relative to similar alcohols.

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* There are obvious exceptions to this broad generalization. It is apparent from the data in Table 1 that ethanol has a lower E_d than methanol because of the relaxation energy. This arises from the higher polarizability of the bulkier ethyl group, which can more readily accommodate the negative charge on the anion. This effect, which is well known, was noted by J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.*, 1970, **92**, 5986.

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