Acidity of Carboxylic Acids: due to Delocalization or Induction?

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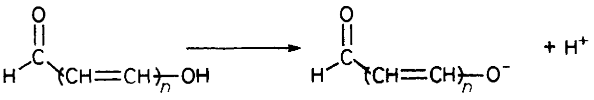
AM1 calculations for vinylogues of formic acid and vinyl alcohol indicate that their acidities can be explained in terms of resonance stabilization of the conjugate anions, as would be expected in terms of current theory.

The fact that carboxylic acids are much more acidic than alcohols has long been attributed to stabilization of the carboxylate anion by delocalization.[1] The corresponding stabilization of the parent acid is expected to be much smaller because it involves separation (sacrificial conjugation) rather than dispersal of charge.

This view has now been challenged by Thomas *et al.*[2a] and Siggel *et al.*[2b,c] who claim on the basis of atomic charges calculated by Bader's[3] formalism that the increased acidity is due mainly, if not entirely, to the inductive effect of the neighbouring carbonyl group in the acid. Here we report a computational study which supports the conventional view, that the acidity of carboxylic acids is due primarily to resonance stabilization of the conjugate anions. Exner[4] has also recently criticized the suggestions made by Thomas *et al.* Our work provides a more definitive refutation.

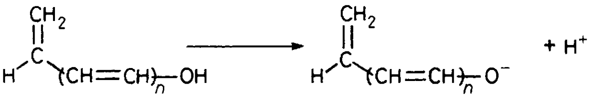


$$\mathrm{HC(=O)\!-\!(CH{=}CH)_{\mathit{n}}\!-\!OH} \longrightarrow \mathrm{HC(=O)\!-\!(CH{=}CH)_{\mathit{n}}\!-\!O^-} + \mathrm{H^+}$$

(1a–d) (2a–d)

$$\mathrm{EtOH} \longrightarrow \mathrm{EtO^-} + \mathrm{H^+}$$

(3) (4)



$$\mathrm{HC(=CH_2)\!-\!(CH{=}CH)_{\mathit{n}}\!-\!OH} \longrightarrow \mathrm{HC(=CH_2)\!-\!(CH{=}CH)_{\mathit{n}}\!-\!O^-} + \mathrm{H^+}$$

(5a–d) (6a–d)

If the acidity of formic acid (**1a**) were due solely to an inductive effect of the carbonyl group, the acidities of vinylogues (**1b**—**d**) of formic acid would be expected to decrease with increasing separation between the carbonyl and hydroxy groups, *i.e.*, the greater the number, *n*, of intervening double bonds. Conversely, if the acidity of (**1**) is due to resonance stabilization of the anion (**2**), acidity should increase with the size of the conjugated system, *i.e.*, with *n*. A knowledge of the relevant deprotonation energies (DPEs) should therefore provide a distinction between the two explanations. Two further factors that have to be considered are the greater electronegativity of sp^2 than of sp^3 hybridized carbon and the stabilizing effect in (**1**) of dividing the negative charge between two oxygen atoms. The following computational study was designed to distinguish between the various effects.

The calculations were carried out using the standard closed shell restricted Hartree–Fock (RHF) version of the AM1[5] method, as implemented in the AMPAC program.† This has been shown[6] to give good estimates of proton affinities (PAs) and DPEs for a wide range of organic molecules, provided that the experimental value is used for the heat of formation of

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† Available from the Quantum Chemistry Program Exchange (QCPE), Program No. 506, Indiana University, Bloomington, IN 47405, U.S.A.

Table 1. Heat of formation,[a] deprotonation enthalpies,[a] and formal charges.

	Heat of formation				
	Neutral	Anion	DPE	DPE (expt.)[7]	g_{O^-} [b]
Formic acid and its vinylogues					
(**1a**) $n = 0$	−97.4	−109.4	355.2	345	−0.61
(**1b**) $n = 1$	−68.2	−100.4	335.0		−0.49
(**1c**) $n = 2$	−54.3	−93.1	328.4		−0.45
(**1d**) $n = 3$	−41.2	−83.4	325.0		−0.42
Ethanol					
(**3**)	−64.2	−45.5	385.9	376	−0.75
Vinyl alcohol and its vinylogues					
(**5a**) $n = 0$	−33.5	−37.2	363.5		−0.60
(**5b**) $n = 1$	−20.5	−39.6	348.1		−0.52
(**5c**) $n = 2$	−7.6	−35.1	339.7		−0.48
(**5d**) $n = 3$	5.3	−27.4	334.5		−0.45

[a] Units: kcal mol^{-1} (1 kcal = 4.184 kJ). [b] Formal charge on oxygen in the anion.

H^+ (the AM1 value is much too small) and that, in the case of DPEs, the negative charge in the conjugate anion is not too localized on a single atom. The latter condition is met in the systems considered here.

We began by studying formic acid (**1a**) and its first three vinylogues (**1b**—**d**). The heats of formation calculated for them and for their conjugate anions (**2a**—**d**) are shown in Table 1, together with the calculated formal charges on oxygen. Experimental values are included where available. Standard AMPAC archive files for all the species studied here are available on request.

Table 1 also shows the DPEs calculated for (**1a**—**d**). These *decrease* along the series (**1a**) > (**1b**) > (**1c**) > (**1d**), implying an *increase* in acidity with chain length. The differences are too large to be attributed to deficiencies of AM1, particularly since the errors in the calculated heats of formation are expected to be similar in such a series of analogous compounds. Our results therefore support the traditional view, that the factor primarily responsible for the acidity of molecules of this kind is resonance stabilization of the conjugate anions. This conclusion is further supported by the prediction that all the corresponding anions have C_{2v} symmetry, the oxygen atoms being equivalent.

As a further check, we carried out analogous calculations for ethanol (**3**) and ethoxide ion (**4**), and for a series of ω-acylenols (**5a**—**d**) and their conjugate anions (**6a**—**d**). The results are shown in Table 1, together with the calculated formal charges on oxygen in the anions. Here again the DPEs of (**5**) fall with increasing chain length and the change with each successive addition of a vinyl group is comparable with that for the formic acid vinylogues (**1**); the values for (**1**)/(**5**) are given in equation (1). This would be expected if the relative acidities in the series (**1a**—**d**), and (**5a**—**d**), are due primarily to resonance stabilization of the conjugate anions. Note also that while the differences for addition of the second and third vinyl groups are less for (**1**) than for (**5**), the reverse is true for addition of the first vinyl group, implying that this leads to a disproportionately large increase in the acidity of (**1b**). Since any inductive contribution would lead to a *decrease* in the acidity of (**1b**) relative to (**1a**), these results provide no indication that inductive effects play any significant role.

$$\begin{aligned}&[n, 0 \rightarrow 1]\ 20.2\ (15.4);\\ &\quad [1 \rightarrow 2]\ 6.6\ (8.4);\\ &\quad [2 \rightarrow 3]\ 3.4\ (5.2)\ \text{kcal mol}^{-1}\end{aligned} \qquad (1)$$

The negative charges in the anions (**2**) are concentrated on the oxygen atoms. The large difference in acidity between (**1a**) and (**1b**) can then be attributed to destabilization of (**2a**) by coulombic repulsion between the negatively charged oxygen atoms. In (**2b**—**d**), the oxygen atoms are further apart, while in (**6a**—**d**) the negative charge is delocalized.

Our results therefore vindicate the traditional explanation for the acidity of formic acid, within the context of the electronic molecular model currently used by organic chemists. It may be that a different model can be constructed in which the effects normally attributed to delocalization are expressed in some other way, *e.g.*, polarization of the intervening carbon chain by the charges on oxygen. However, our calculations do not support any such interpretation and it would in any case involve additional assumptions. This would be sufficient to refute it.‡

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‡ Occam's Razor; *Entia non sunt multiplicanda praeter necessitetem.*