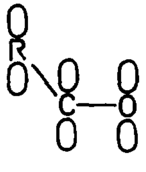
Tetrahedron Letters No.36, pp. 3549-3552, 1967. Pergamon Press Ltd. Printed in Great Britain.

AN LCAO-HMO TREATMENT OF THE ACIDITY OF UNSATURATED CARBOXYLIC ACIDS

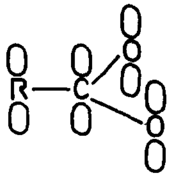
Manfred T. Reetz[*]
Department of Chemistry
University of Michigan, Ann Arbor, Mich. 48104

(Received in Germany 21 June 1967)

Although the classical theories of the acidity of carboxylic acids have been known for some time (1,2), no quantum mechanical treatment has thus far been carried out. In this communication we wish to describe an LCAO-HMO treatment which quantitatively accounts for the relative acidities of unsaturated carboxylic acids. Our approach rests on the assumption that the pK_i of this type of acid is directly proportional to the difference in π-bond energy between the ionized and the unionized acid. We further assume that the effect of the hydroxyl group on the π-energies is constant for all unionized acids (3). Quantum mechanically, we are thus dealing with aldehydic and substituted hetero-allylic systems[**]:



$(E_\pi)_{AH_i}$
Undissociated



$(E_\pi)_{A_i^-}$
Dissociated

Following the usual Hückel approximations (4), we neglect all resonance integrals between atoms which are not directly bonded to each other and set the overlap integral equal to zero. Implicit in this treatment is the assumption that any solvation effects and σ-bond energy changes are constant from one

---

*) Present address: Organisch-Chemisches Institut der Universität Göttingen.

**) Hydrogen bonding effects are thus neglected.

system to another (5). Utilizing Streitwieser's table of suggested parameter values (4), we assign the following values to the Coulomb and resonance integrals: $\alpha_o = \alpha_c + 2\beta$; $\beta_{c-c} = \beta_{c-o}$. Since the π-energy of a compound with n π-electrons has the form $E_\pi = n\alpha + M\beta$, the difference in π-energy between the ionized and the unionized acid, ΔE_{π_i} , is determined by:

$$\Delta E_{\pi_i} = (E_\pi)_{A_i^-} - (E_\pi)_{AH_i} = 2\alpha + \Delta M_i \beta$$

All values for M (and thereby ΔM_i) are calculated from the solutions of the corresponding secular equations. Instead of assigning β an empirical value, we retain it as an adjustable parameter. Our correlation then has the following form

$$pK_i = a + b\Delta M_i$$

in which the empirical slope, b , contains β. Table I and Figure I show the calculated and experimental pK_i values for a number of structurally different acids.

TABLE I

Calculated and Experimental* pK_i Values

Acid	ΔM_i	Calcd. pK_i	Expl. pK_i
Formic acid	4.6358	3.74	3.75
Acrylic acid	4.5264	4.27	4.25
Benzoic acid	4.5446	4.18	4.19
trans-Cinnamic acid	4.5004	4.40	4.44
β-Naphthoic acid	4.5404	4.20	4.17
α-Naphthoic acid**	4.5272	4.27	3.70
cis-Cinnamic acid**	4.5004	4.40	3.89

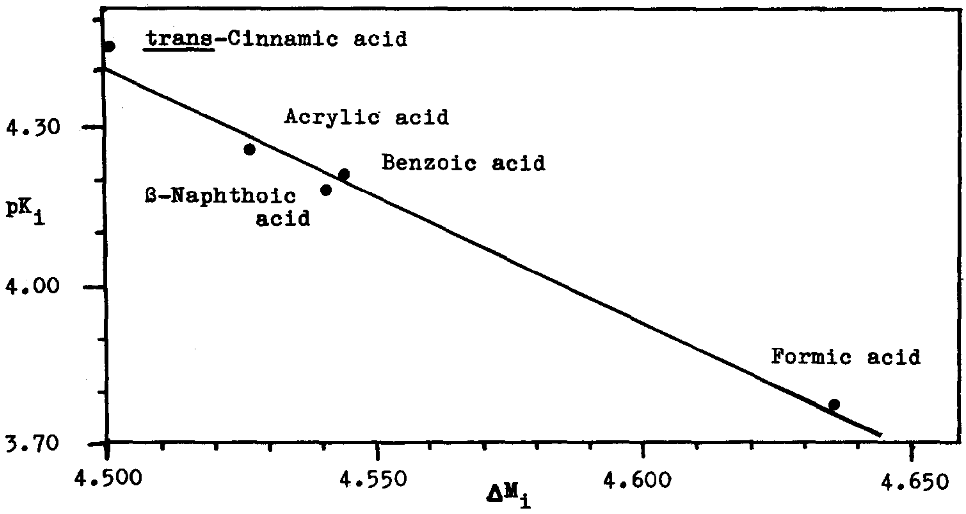
---

*) All experimental pK_i values refer to aqueous solutions, reference (6).

**) Not included in the derivation of the correlation (method of least squares) ; see discussion below.

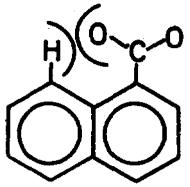
FIG. I

Correlation of Acidities With MO Calculations

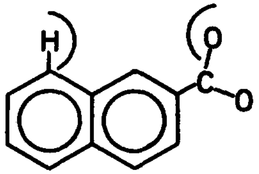


Inspite of the many assumptions, the correlation is surprisingly good. Our treatment thus quantitatively confirms the long held classical view that the introduction of unsaturated substituents in formic acid has an acid weakening effect (1). This phenomenon has been attributed to an electron-donating resonance effect, applying to systems in which the unsaturated substituents are conjugated with the carboxyl group. It has been suggested that an opposing inductive effect, brought about by the $\underline{sp}^2$-hybridized carbon atoms closest to the carboxyl group, to some extent also takes a hand in settling the acid strength, but that it is of the same order of magnitude for olefinic as for benzenoid unsaturation (1). A rough approximation of the magnitude of this effect can be obtained by considering a correlation derived from unsaturated acids to the exclusion of formic acid. Since the constant inductive effect present in unsaturated acids does not apply to formic acid, such a correlation should therefore predict a calculated pK_i which is lower than the experimental value. This is indeed the case. The newly calculated pK_i of formic acid, 3.60 , is 0.14 pK units lower than the previously calculated value.

That the calculated pK_i of α-naphthoic acid is higher than the experimental value is to be expected on the following grounds: The steric effect of the peri hydrogen atom forces the carboxyl group out of the plane of the aromatic ring, thereby disturbing the effective conjugation between the two groups. This effect is absent in the isomeric ß-naphthoic acid, as reflected by the close agreement between calculated and experimental pK_i values (Table I):



α-Naphthoic acid



β-Naphthoic acid

It is interesting to note that the inductive effect, which remains unaffected by the above steric considerations, can potentially gain the upper hand. This seems to be the case with α-naphthoic acid, which is slightly more acidic than formic acid. Similar steric arguments involving the interaction between the phenyl and the carboxyl groups apply to *cis*-cinnamic acid.

The author would like to thank Prof. L.S. Bartell for his stimulating comments. Special acknowledgment regarding technical assistance with the computer program is due to Mr. W.K. Li and Mr. J.E. Dunning.

REFERENCES

1. C.K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, 1953.
2. E.S. Gould, *Mechanism and Structure in Organic Chemistry*, Henry Holt and Company, Inc., New York, 1959.
3. For a discussion of the effect of hydroxyl groups on the energy of π-systems see the following: S.F. Mason, *J. Chem. Soc.*, 674, 1958 ; M.G. Evans, *Trans. Faraday Soc.*, **45**, 312, 1949.
4. A. Streitwieser, *Molecular Orbital Theory for Organic Chemists*, John Wiley and Sons, Inc., New York, 1961.
5. A. Streitwieser, *Tetrahedron Letters*, **6**, 23, 1960.
6. G. Kortüm, W. Vogel, and K. Andrussow, *Dissociation Constants of Organic Acids in Aqueous Solution*, International Union of Pure and Applied Chemistry, Butterworths, London, 1961.