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Ionic Dissociation. I. A Hückel Molecular-Orbital Treatment of the Dissociation of Carboxylic Acids and Several Azine Compounds

Hiroko YAMABE, Teijiro YONEZAWA and Hiroshi KATO[*1]

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto

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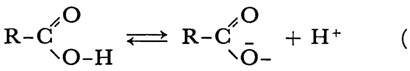
The relationship between the pK_a value and the change in the electronic energy, ΔE, in the course of the dissociation, and the electronic structure of various mono-carboxylic acids and several azine compounds are discussed on the basis of the calculation by Hückel methods for σ and π electron systems. The parallelism between the pK_a and the calculated ΔE of the acids is observed. The σ electron densities of the -COOH proton and the O^- lone pair, which is constituted by the released electron on the dissociation, run parallel with the pK_a's. The delocalizability of the lone pair for the electrophilic reaction, and that of the proton for the nucleophilic reaction, have a linear relationship with the pK_a's. Similar relations are seen in several azine compounds. Therefore, it may be said that the protonation will take place by means of the electrophilic attack at the lone pair, and that the deprotonation occurs by means of the nucleophilic attack at the proton.

It is said that the strength of an acid depends on the relative stabilities of it and its anion.1) The dissociation constant, pK_a, of conjugated acids and bases has been related to the change in π electronic energy in the course of the dissociation, and to the charge of the protonated heteroatom in these compounds.2-4) However, as one of us has pointed out in a previous paper,5) only a classical electrostatic theory6) has been proposed in connection with the dissociation of saturated compounds, except for our previous calculation on the α-amino acids.5) In this paper we will report the relationship between the value of pK_a and the change in the electronic energy, ΔE, and in other quantities of the electronic structures of various mono-carboxylic acids and several bases; our findings are based on the calculation by the Hückel method for σ and π systems.

The distinguishing characteristic of this work is the model it employed; in it the mechanism of the dissociation is taken into account in a simple way. Namely, the carboxylic acid is considered to be dissociated according to Eq. (1):



$$\mathrm{R{-}C}\begin{smallmatrix}{/\!\!/}\mathrm{O}\\ \backslash\mathrm{O{-}H}\end{smallmatrix} \rightleftarrows \mathrm{R{-}C}\begin{smallmatrix}{/\!\!/}\mathrm{O}\\ \backslash\mathrm{O^{-}}\end{smallmatrix} + \mathrm{H^+}$$

(1)[*2]

The following model is assumed: in the anionic form, electrons released by the dissociation of the proton constitute, in a sense, a new lone pair of the oxygen delocalize over a whole molecule. This will be denoted as "the O^- lone pair" through-out the present paper. A recombination reaction to the left-hand side of Eq. (1) will take place by means of the attack of the dissociated proton (or a hydronium ion) on the O^- lone pair. The electron density of this lone pair is evaluated by the Hückel method for various acids.

After these comparative discussions, the following conclusion was obtained. There is a rough linearity between the pK_a value and the calculated ΔE value. The σ electron density of the O^- lone pair and the delocalizability,6) D_r^{E}, for the electrophilic reaction of the O^- lone pair run parallel with the pK_a value, as well as with the σ electron density and the delocalizability,6) D_r^{N}, for the nucleophilic reaction of the hydrogen atom of a carboxylic group. Further, similar relations are seen in azine compounds as will be described in detail later. Therefore, the protonation seems to take place by means of the electrophilic attack at the lone pair, while

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[*1] Present address: Department of General Education, Nagoya University, Chikusa-ku, Nagoya.

1) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," The Clarendon Press in the University of Oxford (1949), Chapter VI.

2) H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 275 (1950); T. Nakajima and A. Pullman, *J. Chim. Phys.*, **1958**, 737.

3) M. T. Reets, *Tetrahedron Lett.*, **1967**, 3549.

4) J. D. Vaughan, D. G. Fullerton and C. A. Chan, *Intern. J. Quantum Chem.*, **II**, 205 (1968).

5) T. Yonezawa, G. Del Re and B. Pullman, This Bulletin, **37**, 985 (1964).

6) K. Fukui, H. Kato and T. Yonezawa, *ibid.*, **34**, 1111 (1961).

[*2] The existence of the H_2O molecules and the hydration effect in the dissociation process are not taken into account.

the deprotonation seems to occur by means of the nucleophilic attack at the proton.

Calculations

The electronic energy change, ΔE, in the course of dissociation is due to the difference between the total energy of the final and the initial states in Eq. (1). This equation is adopted for a series of carboxylic acids, and the calculation of ΔE is performed according to the following formulae:[5)]

$$\Delta E = E_\sigma(\text{final}) - E_\sigma(\text{initial}) - \sum_\mu \frac{Q_{\rm H} Q_\mu e^2}{R_{{\rm H}\mu}}$$

$$\Delta E_\sigma = E_\sigma(\text{final}) - E_\sigma(\text{initial}) \qquad (2)$$

Here, E_σ(initial) and E_σ(final) denote the energies of the protonated compounds and of the conjugate base respectively. The third term corresponds to the electrostatic interactions between the dissociable proton and the other atoms in the protonated compounds. $Q_{\rm H}$ is the net charge (in e units) of the proton, Q_μ is the net charge of the μ-th atom, and $R_{{\rm H}\mu}$ is the distance between them. The calculation of $R_{{\rm H}\mu}$ is carried out using a formula proposed by Eyring[7)] and by Kirkwood and Westheimer.[8)] The precise interpretation of Eq. (2) was given in a previous paper.[5)] In that paper,[5)] the variation in the total π electron energy is assumed to be constant. In this work we confirmed this by the performance of the Hückel calculation.[*3]

For the determination of the electronic energy and the electron distribution of σ and π electron systems, the Hückel approximation is employed. The parameters used in these calculations are tabulated in Table 1.

Results and Discussions

The electronic structures of σ and π electron systems are obtained for various acids. As an example, the σ-electron distribution of the CH_3COOH, CF_3COOH, and C_3H_5COOH molecules and their anions are shown in Fig. 1, together with the π electron distribution. In the anionic form, about 93% of the lone-pair electrons localize at the oxygen atom. Furthermore, the highest occupied orbital localizes largely at the O^- lone pair; that is, it becomes a lone-pair MO.[*4] The results of the calculation are listed in Table 2, together with the experimantal values of pK_a for a series of carboxylic acids. In Table 2, ΔE_σ gives the variation in the total σ electronic energies in the course of the dissociation

Table 1. Parameters for the Hückel calculation

Coulomb integrals for σ systems		Resonance integrals for σ systems	
C(sp^3 hybridized)	α	C–C (sp^3-sp^3)	β
C(sp^2 hybridized)	$\alpha+0.1\beta$	C–C (sp^2-sp^2)	1.2β
H	$\alpha-0.2\beta$	C (sp^3)	0.34β
=O	$\alpha+0.3\beta$	C (sp^2) *	0.4β
-O-	$\alpha+0.3\beta$	N	0.3β
		O	0.3β
N	$\alpha+0.2\beta$	C–N	β
F	$\alpha+0.9\beta$	C–H	1.1β
Cl	$\alpha+0.5\beta$	O–H	1.2β
Br	$\alpha+0.54\beta$	N–H	1.1β
I	$\alpha+0.5\beta$	C=O	1.2β
		C–O	0.7β
		C–F	0.5β
		C–Cl	0.65β
		C–Br	0.58β
		C–I	0.53β

Coulomb integrals for π systems		Resonance integrals for π systems	
C(in -C=O)	$\alpha+0.2\beta$	C=O	1.4β
=O	$\alpha+2\beta$	C–O (in -COO$^-$)	β
-O(in COO$^-$)	$\alpha+\beta$	C–OH	0.7β
-OH	$\alpha+0.6\beta$	C–NH$_2$	0.6β
-NH$_2$	$\alpha+0.4\beta$		

Hyperconjugation is ignored.

* Resonance integrals between two σ orbitals belonging to the same atom.

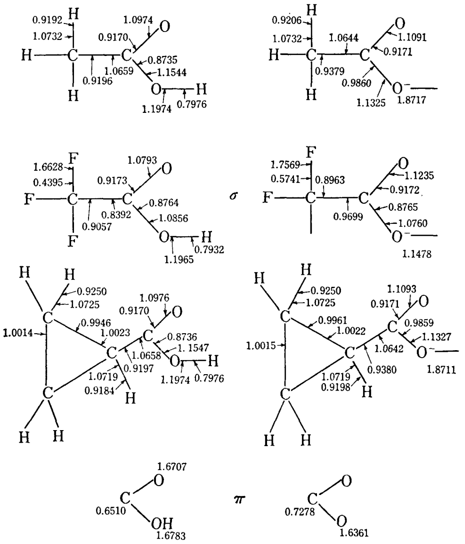

Fig. 1. σ and π electron distribution of some acids.

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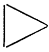
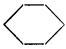
7) H. Eyring, *Phys. Rev.*, **39**, 746 (1932).

8) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506, 513 (1938).

[*3] ΔE_π is calculated as 1.1277 β_π for all the acids except benzoic acid, for which the ΔE_π value is 1.1400 β_π.

[*4] In the extended Hückel calculation of the CH_3COOH molecule, the highest occupied MO is a σ orbital. Moreover, the atomic orbital population of the x direction, which is one component of the lone pair, of the oxygen atom is considerably increased compared with that of the CH_3COOH molecule. Therefore, this MO has the character of a lone-pair MO.

TABLE 2. CALCULATED RESULTS AND OBSERVED pK_a VALUES

Compound	Obs.[a)] pK_a	Calc.						
		ΔE_σ $(-\beta)$	$\sum_\mu \frac{Q_H Q_\mu e^2}{R_{H\mu}}$ (eV)	$\Delta E_\sigma - \sum_\mu \frac{Q_\mu Q_\mu e^2}{R_{H\mu}}$ (eV)	D_r^N	D_r^E	Q_H	Q_L
HCOOH	3.75	1.9004	−0.051	11.454	1.0893	6.4988	0.79786	1.8786
CH_3COOH	4.76	1.8981	−0.075	11.464	1.0951	6.4480	0.79763	1.8717
CH_3CH_2COOH	4.87	1.8980	−0.158	11.546	1.0956	6.4439	0.79761	1.8711
$CH_3(CH_2)_2COOH$	4.82*	1.8980	−0.228	11.616	1.0957	6.4435	0.79761	1.8710
NH_2COCH_2COOH	3.64	1.8977	−0.012	11.398	1.0965	6.4339	0.79757	1.8704
CH_3COCH_2COOH	3.58	1.8977	0.004	11.382	1.0963	6.4358	0.79757	1.8704
FCH_2COOH	2.57	1.8945	0.109	11.258	1.1012	6.3398	0.79725	1.8587
$ClCH_2COOH$	2.87	1.8962	0.073	11.304	1.1014	6.3916	0.79737	1.8655
$BrCH_2COOH$	2.90	1.8960	0.096	11.280	1.1027	6.3847	0.79735	1.8645
ICH_2COOH	3.16	1.8959	0.117	11.258	1.1034	6.3813	0.79734	1.8639
$Cl_2CHCOOH$	1.25	1.8925	0.220	11.135	1.1216	6.2810	0.79695	1.8516
F_3CCOOH	0.23	1.7939	0.668	10.094	1.1070	3.0779	0.79317	1.1478
Cl_3CCOOH	0.66	1.8836	0.376	10.926	2.3693	5.9978	0.79616	1.8084
-COOH	4.83*	1.8981	−0.262	11.650	1.0956	6.4474	0.79764	1.8711
-COOH	4.79*	1.8977	−0.330	11.716	1.0966	6.4363	0.79758	1.8701
-COOH	4.99*	1.8978	−0.275	11.662	1.0963	6.4395	0.79760	1.8704
-COOH	4.90*	1.8978	−0.259	11.646	1.0964	6.4386	0.79760	1.8703
-COOH	4.18*	1.8957	−0.309	11.683	1.0990	6.3542	0.79685	1.8683

pK_a values are observed at the temperature from 18°C to 25°C.

a) A. Albert and E.P. Serjeant "Ionization Constants of Acids and Bases," Methuen & Co. Ltd., London.

* G. Kortum, W. Vogel and K. Andrussow "Dissociation Constants of Organic Acids in Aqueous Solutions," Butterworths, London, 1961. The dissociation constant in this book is converted to pK_a.

in units of $-\beta$ and eV's respectively, where we have chosen 6 eV for $-\beta$.5),[*5] D^N_r indicates the values of delocalizability6) for an electrophilic reaction at the hydrogen atom of a -COOH group. D^E_r is the delocalizability8) for an electrophilic reaction at the O^- lone pair of a $-COO^-$ group. Q_H and Q_L give the electron densities of the H of a -COOH group and the O^- lone pair of a $-COO^-$ group respectively. From Table 2, a parallelism between the pK_a values and ΔE_σ's is observed, though the values of ΔE_σ's[*5] themselves are not very different for various acids. However, large deviations in CCl_3COOH and CF_3COOH from a linear relationship are seen.

In Fig. 2, the values of pK_a are plotted against ΔE(in eV),[*6] which is given by Eq. (2). Including the electrostatic interaction term[*7] of $Q_H Q_\mu e^2/R_{H\mu}$ the deviation in CCl_3COOH and CF_3COOH is greatly improved, as may be seen in Fig. 2 and Table 2.[*8] This indicates that the CCl_3 and CF_3 groups in these compounds are very electronegative and they attract the dissociable hydrogen, which is in agreement with Dewar's description.[*9] This effect will make an acid weaker than would be expected from the calculated ΔE_σ value. Further-

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[*5] Only the relative values of ΔE_σ for the various compounds have meaning. There is some arbitrariness in the selection of the value of $-\beta$.

[*6] The absolute value of ΔE can not be discussed.

[*7] In Table 2, the following relation is noted: as the electrostatic interaction with the dissociable hydrogen, $\sum = Q_H Q_\mu e^2/\mu R_{H\mu}$ increases, the pK_a value decreases.

[*8] CF_3COOH is not included in Fig. 2 because the deviation in CF_3COOH is still large. Possibly this deviation is due to the extraordinarily heteroritic property of the three F atoms.

[*9] Dewar describes in his book (Ref. 1) that "in acids containing a highly polar group in proximity of the dissociable hydrogen, a direct electrostatic attraction or repulsion of the nascent proton may increase or decrease the dissociation energy."

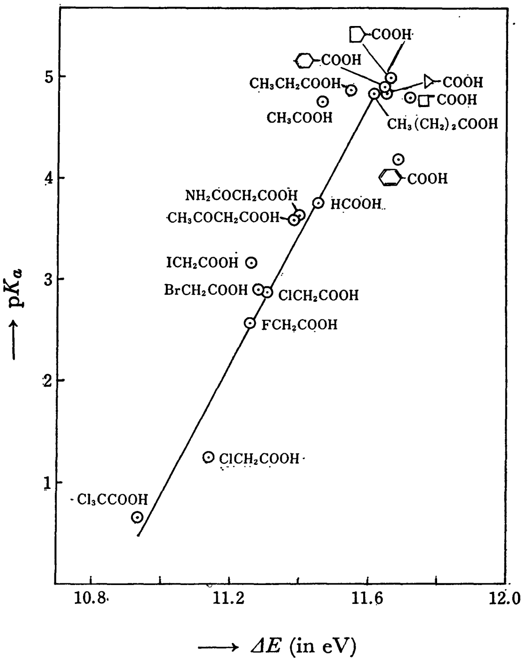

Fig. 2. The dissociation constant pK_a *vs.* ΔE, where $\Delta E=\Delta E_\sigma-\sum_\mu Q_H Q_\mu e^2/R_{H\mu}$.

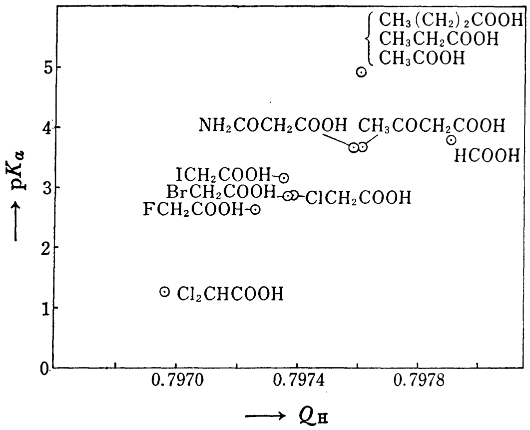

Fig. 3. The dissociation constant pK_a *vs.* Q_H of acids.

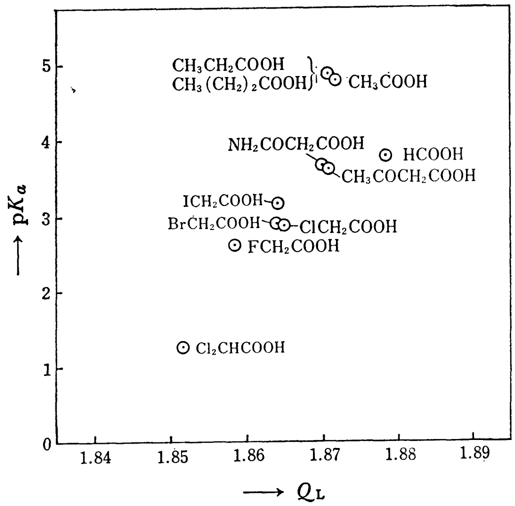

Fig. 4. The dissociation constant pK_a *vs.* Q_L of acids.

more, in Fig. 2 the difference in the values of ΔE for various acids become larger than in the case of ΔE_σ's. That is it may be noted that the electrostatic interaction term contributes to the relative acidity of the acids.

On the basis of these calculations, it may be said that ΔE_σ's calculated by Hückel method run parallel with the pK_a values for the compounds having not so polar a group. As for the molecule having a highly polar group, the contribution of the electrostatic interaction term to its acidity should not be ignored. Furthermore, it may be concluded that the acid dissociates more easily when its anion is more stable than that of the parent acid.

Also, a very rough linear relation is seen between the pK_a and D_r^N and the electron density of the hydrogen, Q_H. It is plotted in Fig. 3.*[10] This means that the dissociable hydrogen may be attacked in a nucleophilic fashion by the H_2O molecule to give the $RCOO^-$ and H_3O^+ ions in the dissociation process. Also the $D^E{}_r$ and the electron density of the O^- lone pair of the anion Q_L run parallen with the pK_a. It is plotted in Fig. 4.*[10] This means that the ion recombination takes place by means of the attack on the O^- lone pair by the hydrogen atom of the H_2O molecule. These results suggest that the model employed here is plausible; that is, the electron released on the dissociation constitutes a new lone pair of O^- of the anion and delocalize over the whole molecule.

Dissociation of Azine Compounds

In the preceding part of this paper we found that, as far as we have treated, the ΔE_σ calculated by the Hückel method runs parallel with the pK_a value for the carboxylic acids having not so highly a polar group. Next, we will examine whether this relation holds in the cases of several azines,*[11] though the azines calculated in the present work are few in number.

The dissociation equilibrium is assumed to be in the form of Eq. (3), in which pyridine is taken as an example.

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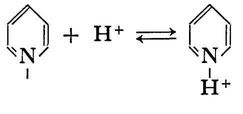
*[10] In Fig. 4 and Fig. 5, CF_3COOH and CCl_3COOH are not included.

*[11] The interrelation between the ΔE_π and the pK_a values of some of these compounds has been discussed by several authors (Ref. 2).

TABLE 3. CALCULATED RESULTS AND THE OBSERVED pK_a VALUES* FOR SOME AZINE COMPOUNDS

Compound	pK_a	ΔE_σ (in $-\beta$)	$D_H{}^N$	$D_L{}^E$	Q_H	Q_L
Pyridine	5.23	1.7544	1.1579	10.8848	0.8345	1.7523
Pyrazine	0.6	1.7378	1.1547	11.2164	0.8351	1.7559
Pyrimidine	1.3	1.7394	1.1521	11.7104	0.8357	1.7581
Pyridazine	2.33	1.7493	1.1347	18.7290	0.8421	1.7708

* A. Albert and E.P. Serjent "Ionizationts of Acids and Bases." Methuen Co. Ltd, London.



(3)

The value of ΔE_σ is evaluated according to Eq. (4):

$$\Delta E_\sigma = E_\sigma(\text{protonated form}) - E_\sigma(\text{unprotonated form}) \quad (4)$$

The method of the calculation and the parameters employed are similar to those use for the carboxylic acids.

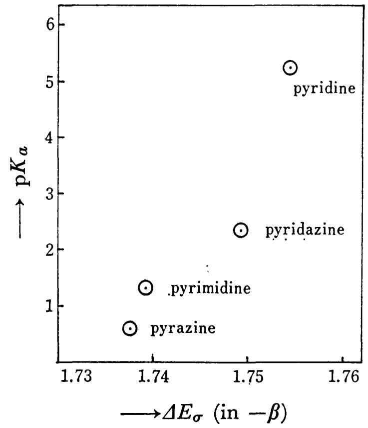


Fig. 5. The dissociation constant pK_a *vs.* ΔE_σ.

The calculated ΔE_σ values are shown in Table 3, together with the observed pK_a values; they are plotted in Fig. 5.*[12] A parallelism between ΔE_σ and the pK_a of azines is observed.

In diazines it is observed that, in the anionic form, the electron density of the N lone-pair Q_L and the delocalizability, $D_L{}^E$ of that lone pair for the electrophilic reaction run parallel with the pK_a.*[13] Also, in the protonated form the electron density of the hydrogen, Q_H, and the delocalizability, $D_H{}^N$, of that proton for the nucleophilic reaction run parallel with the pK_a in diazines. This means that the protonation takes place by the attack on the N lone pair in Eq. (3) and that the deprotonation is induced by such a molecule as H_2O, which attacks the proton. These circumstances were observed previously in the case of acids.

An approximate linear relation between the pK_a value and the energy change, ΔE, of the acids and bases can naturally be expected. However, the coarse linearity obtained in the present work for some acids and bases seems to be a change result of the appropriate selections of the molecules to be calculated, the method of the approximation, and the various parameters. When the peculiarity of each molecule, which is induced by each substituent, the steric factor, and so on, can not be taken into account in the parameters, the linearity will not be obtained and some corrections for the calculation are needed. An example of the deviation caused by the steric factor has been reported in the calculation of the π energy change in the dissociation of the conjugated acids.[3)]

The calculations were carried out on a HITAC 5020 computer at the computation center of the University of Tokyo.

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*[12] The σ electron densities of the azines have been presented in one of our previous papers (Ref. 9).

*[13] The paralellism between the σ electron density of the N lone pair of diazine and the blue shifts of n–π^* bands, accompanied by the change in the solvent from cyclohexane to aqueous solution, has been reported in our previous paper (Ref. 9).

9) T. Yonezawa, H. Yamabe and H. Kato, This Bulletin, **42**, 76 (1969).