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Ionic Dissociation. II. An Extended Hückel Treatment of the Dissociation of Pseudo Acids

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The electronic structures of several pseudo acids are studied, in connection with their reactivity and stability, by the Extended Hückel method. The linear relationship between the observed pK_a value and the change in the calculated electronic energy, ΔE, in the course of the dissociation of the pseudo acids is also observed. The order of the stability of the carbanion, referred to its parent acid, as estimated from our calculations, is; $CH_2NO_2^- > CH_2COCH_3^- > CH_2CN^-$. Di- or tri- substituted carbanions should be more stable. This order is parallel with that of the electron-attracting abilities of the groups adjacent to the methylene group. The highest-occupied MO of the carbanion is remarkably unstable, resembling a lone-pair level, and the atomic orbital population of that MO is large at the P_z AO of the carbon. This reflects the high reactivities of the carbanion as a reaction intermediate; the electrophilic addition probably takes place at the carbon atom.

Carbanions are known as important intermediates in many organic and biological reactions,[1] especially in various condensations such as those of the aldol-type. The more easily the carbanion is generated, and the more stabilized it is, the more enhancement of the reaction may be expected. Therefore, it would be significant to ascertain what kinds of carbanions satisfy these conditions.

Studies of the carbanions have been carried out by many authors. Especially, there are many reports by Cram *et al.*[2] paying particular attention to their sterochemistry. However, as far as we know, there have been few discussions of the stabilities and the reactivities of the carbanions,

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1) L. L. Ingraham, "Biochemical Mechanics", John Wiley & Sons, Inc., New York (1962), Part Two, Codensation. M. J. S. Dewar, "The Electronic Theory of Organic Chemistry", The Clarendon Press in the University of Oxford (1949), Chapter VII.

2) D. J. Cram, A. Langemann, J. Allinger and K. R. Kopecky, *J. Amer. Chem. Soc.*, **81**, 5740 (1959) and subsequent several papers.

on the basis of the calculated electronic structures. Nagakura *et al.*[3] studied the dissociation of pseudo acids from the spectroscopic point of view and discussed their π electronic structures. However, they did not refer to the stability and reactivity of the carbanions.

In this paper, as one of a series of studies of the ionic dissociation,[4] we will report some findings on the electronic structures, including the π and σ electronic systems, of some pseudo acids which dissociate in water as in Eq. (1) and which give carbanions.

$$\mathrm{HA} \rightleftarrows \mathrm{A}^- + \mathrm{H}^+ \qquad (1)^{*2}$$

Also the relationship between $\mathrm{p}K_a$[5] and the change in the calculated electronic energy, ΔE, in the course of dissociation (Eq. (1)) will be presented.

Calculations

The electronic energy and the electronic structure of the molecule and its anion were calculated by using the Extended Hückel method proposed by Hoffmann,[6] in which all the valence atomic orbitals (AO) are taken into account. For the coulomb integrals, H_{rr}, the following valence-state ionization potentials (eV) for the hydrogen, carbon, oxygen, and nitrogen have been used:

$H_{rr}(\mathrm{H1S}) = -13.6$ $\quad H_{rr}(\mathrm{C2S}) = -21.43$
$H_{rr}(\mathrm{C2P}) = -11.42$ $\quad H_{rr}(\mathrm{O2S}) = -35.30$
$H_{rr}(\mathrm{O2P}) = -15.45$ $\quad H_{rr}(\mathrm{N2S}) = -27.50$
$H_{rr}(\mathrm{N2P}) = -14.49$

The resonance integrals, H_{rs}, have been calculated by means of $H_{rs} = (1/2)KS_{rs}(H_{rr} + H_{ss})$, where $K = 1.75$[6] and where S_{rs} is the overlap integral between the rth and sth AO's. The electronic energy change, ΔE, in the dissociation process is estimated by means of the difference of the calculated total electronic energy as follows:

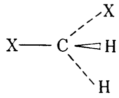
$$\Delta E = E(\mathrm{final}) - E(\mathrm{initial}) \qquad (2)$$

The bond lengths employed are given in Table 1. The bond angles are assumed to be as follows: $\angle$ONO in CH_3NO_2: 127°; for a sp^2 carbon, 120°, and for a sp^3 carbon, 109.5°. The Z axis is chosen in the direction of the π orbital. The calculation of the final state as an anion is made in the configuration of the sp^2 hybridization of the methylene carbon (abbreviated hereafter as the sp^2 configuration). For the anions of CH_3NO_2 and CH_4, two anionic forms, the sp^3 and sp^2 configurations, are calculated. As it is revealed that the sp^2 configuration is more stable for these molecules, the sp^2 configuration is adopted as the final anionic form of the other molecules.

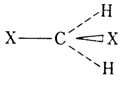
TABLE 1. INTERATOMIC DISTANCES (Å)

C-H	1.09
N-O (in CH_3NO_2)	1.21
C-N (in CH_3NO_2)	1.46
C-N (in CH_3CN)	1.16
C-C (in CH_3CN)	1.46
C-C (in CH_3COCH_3)	1.54
C-O (in CH_3COCH_3)	1.22

For $CH_2(NO_2)_2$, the cofiguration (1) is adopted; in our calculations it is slightly stable than the other configuration (2).

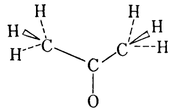


(1)



(2)

In both (1) and (2), X denotes the NO_2 substituent and the central carbon has an sp^3 hybridization.[*3] One of the reasons for this seems to be a rather large π-conjugation in the X-C bond of the configuration (1). For CH_3COCH_3, the following configuration is assumed, in which the central carbon has an sp^2 hybridization:



Results and Discussion

As many authors have pointed out, the charge distribution calculated by this method is unrealistic. Therefore, the absolute values of the electron densities and the energy levels have little meaning. However, the trend of their variation in a series of molecules may be discussed meaningfully. The calculated results are given in Table 2, together with the observed values of $\mathrm{p}K_a$. The values of $\mathrm{p}K_a$ are plotted against ΔE (eV) for various pseudo acids as in Fig. 1. A linear

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3) S. Nagakura, *Mol. Phys.*, **1960**, 152; F. Hashimoto, J. Tanaka and S. Nagakura, *J. Mol. Spectry.*, **10**, 401 (1963).

4) T. Yonezawa, G. Del Re and B. Pullman, This Bulletin, **37**, 985 (1964). T. Yonezawa, H. Yamabe and H. Kato, "Ionic Dissociation I. A Hückel Molecular-Orbital Treatment of the Dissociation of Carboxylic Acids and Some Bases," (to be published in this Bulletin).

[*2] The presence of the H_2O molecule and its effect on the dissociation process is not taken into account in the present work.

5) P. G. Pearson and A. L. Dillon, *J. Amer. Chem Soc.*, **75**, 2439 (1953).

6) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

[*3] The configurations (1) and (2) are apparently different, because the substituent $\mathrm{N}\langle^{\mathrm{O}}_{\mathrm{O}}$ is not spherical.

TABLE 2. CALCULATED ΔE AND OBSERVED pK_a VALUES

Compounds	Obsd.5) pK_a	Calcd. ΔE (eV)
CH_4	40	6.783
CH_3NO_2	11	5.006
$CH_2(NO_2)_2$	4	4.576
$CH(NO_2)_3$	0	4.468
CH_3CN	25	5.876
$CH_2(CN)_2$	12	5.368
$CH(CN)_3$	0	5.011
CH_3COCH_3	20	5.791

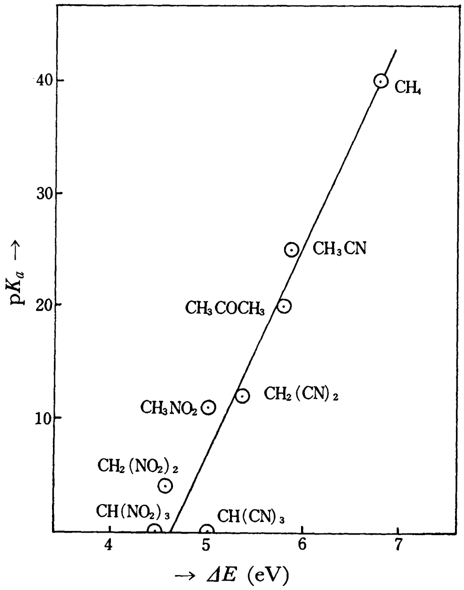

Fig. 1. The dissociation constant pK_a *vs* ΔE.

relationship between the pK_a's and the ΔE's is observed. That is the pseudo acid is ionized more easily as the ΔE is smaller. Therefore, the order of the stability of the carbanion referred to its parent acid, as estimated from our calculations, should be:

$$CH_2NO_2^- > CH_2COCH_3^- > CH_2CN^-$$

and di- or tri- substituted carbanion should be more stable still. On the other hand, the common order of the electron-attracting abilities of the groups adjacent to the methylene group is $NO_2 > CO > CN$. This order is also confirmed by the population analysis in our calculation to be $NO_2 > COCH_3 > CN$. Therefore, it can be said that the greater the ability of the substituent to bear a negative charge generated in the carbanion, the more stable is the carbanion to the parent acid and the smaller is the pK_a value of the parent acid.

Next we would like to give a detailed discussion of the electronic structure and energy levels of CH_3NO_2, picked as an example from the obtained results. In Fig. 2, atomic populations are given for the parent acid, CH_3NO_2 (I), and the anionic form, $CH_2NO_2^-$, in the sp^3 (II)[*4] and sp^2 (III) configurations. The coordinate axes and the numbering of the three H atoms are also shown. The C atoms of CH_3NO_2 (I) and $CH_2NO_2^-$(II) have an sp^3 hybridization, and that of $CH_2NO_2^-$ (III) has an sp^2 hybridization. The NO_2 group is in the x-y plane, and $CH_2NO_2^-$(III) is planar. It may be seen that an electron released by the dissociation of the proton delocalizes on a whole molecule. The total electronic energy and the π atomic orbital population of the P_z AO in the highest occupied (HO) orbitals are shown in Table 3. In Table 3 and Fig. 2 it may be observed that, in spite of the delocalization of an electron released on a whole molecule, the π atomic orbital population of the p_z AO of the carbon atom C(Z) in the highest occupied orbital of the anion, which is a frontier orbital for the electrophilic attack,7) becomes much larger than that of the parent acid. This means that the electrophilic addition must take place at the carbon atom; this is in agreement with the experimental suggestion.

Furthermore, the energy levels adjacent to the HO level and the lowest unoccupied (LU) level are illustrated in Fig. 3. The qualitative correlation between the energy levels of CH_3NO_2 (I) and its anion is studied. The third highest occupied MO (denoted by C–H in Fig. 3) of CH_3NO_2 (I) is considerably localized at the C–H_3 bond[*5] to be dissociated[*3]. This C–H level corresponds to the HO level of the anion. (See the dotted line in Fig. 3.) These levels of the anions are remarkably unstable and seem to resemble a lone-pair level in which almost one electron localizes at the P_z AO of the carbon (See Table 3). This reflects the high reactivities of a carbanion as a reaction intermediate. The features of the elctronic structure and the energy levels of CH_3-NO_2 and $CH_2NO_2^-$, which have been described above, are also seen in the cases of CH_4 and CH_3^- in the sp^3 and sp^2 configurations.

It is said that such carbanions as $CH_2NO_2^-$ and CH_2CN^- planar and π electron systems must develop a whole molecule. When the configuration of a carbanion, $CH_2NO_2^-$, is changed from an sp^3 to an sp^2, the following variations in

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[*4] In our calculations, the anionic form induced by the dissociation of the H_3 of CH_3NO_2 (I) becomes more stable than that induced by the dissociation of the H_1. The stable form is shown in Fig. 2 as CH_3NO_2 (II).

[*5] The MO coefficients of the s, p_x, p_y and p_z AO's of the atoms C and H_3 in this level are as follows: C(s: -0.001, p_x: 0.028, p_y: 0.000, p_z: -0.565), H_3 (s: -0.437)

7) K. Fukui, T. Yonezawa, C. Nagata and H. Shingu, *J. Chem. Phys.*, **22**, 1433 (1954).

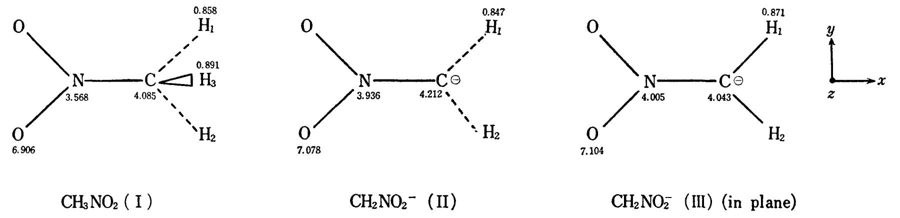

Fig. 2. Atomic populations of CH_3NO_2(I) and its anions are shown. The coordinate axis and the numbering of the three H atoms are also shown. The C atoms of CH_3NO_2(I) and $CH_2NO_2^-$(II) have an sp^3 hybridization, and that of $CH_2NO_2^-$(III) has an sp^2 hybridization. The NO_2 group is in the x-y plane and $CH_2NO_2^-$(III) is planar.

Table 3. Total electronic energy and the atomic orbital population of the P_z AO and that in the highest occupied MO

Compounds		CH_3NO_2(I)	$CH_2NO_2^-$(II)*	$CH_2NO_2^-$(III)*
Total electronic energy (eV)		−493.71	−487.92	−488.70
Atomic orbital population of the P_z AO in the H.O.**	C(z)	0.004	0.970	0.966
	N(z)	0.000	0.369	0.446
	O(z)	0.000	0.264	0.294
Atomic orbital pop. of the P_z AO	C(z)	1.059	1.068	1.009
	N(z)	0.815	1.198	1.274
	O(z)	1.661	1.832	1.858

* $CH_2NO_2^-$(II), $CH_2NO_2^-$(III) denote the sp^3 and the sp^2 configuration, respectively.
** Highest occupied level

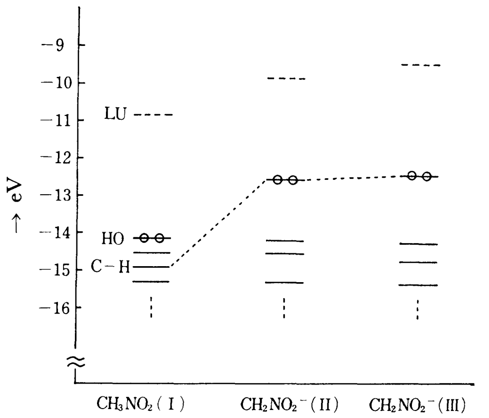

Fig. 3. Energy levels adjacents to the highest occupied level(HO) and the lowest unoccupied level(LU). C-H denotes the level, of which MO is considerably localized at the C-H bond to be dissociated. The dotted line shows the correspondence between the C-H level and HO of the anions.

the energy and the population are observed in our calculations:

1. An electron released is much delocalized over a whole molecule. That is the π conjugation strongly prevails.
2. The total electronic energy becomes lower in an sp^2 than in an sp^3. That is a carbanion treated here becomes more stable in the sp^2 configuration.
3. The highest occupied level becomes higher. That is, a carbanion becomes more reactive.

These results indicate that the configuration of the carbanion will be changed from the sp^3 to the sp^2 by the dissociation of the proton.

As for the electronic transition of the carbanion Nagakura *et al.*[3)] observed that the ultraviolet absorption spectrum of the carbanion has a strong band at wavelengths longer than in the parent pseudo acid; they ascribed this to the intramolecular charge transfer band of the anion. In the present calculations, too, the π-π^* transition energy of the anion is certainly smaller than that of the neutral molecule. However, we can not discuss the electronic transition in more detail, for the approximation of our calculation is very rough.

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