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A CORRELATION BETWEEN THE ACIDITY AND HYBRIDIZATION IN NON-CONJUGATED HYDROCARBONS

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Abstract—Acidity of several non-conjugated hydrocarbons has been studied using the scaled maximum overlap method. It is shown that hybridization has a marked influence on the proton acidity. This effect is most pronounced in hydrocarbons with localized bonds. The straight line correlating proton acidities with s-characters of the corresponding hybrids reads as follows: $pK = 83{\cdot}12 - 1{\cdot}33\ (s\%)$.

THE definition of acids as species showing the tendency to lose a proton,[1] makes possible quantitative comparison between experimentally and theoretically obtained values. Thus Wheland[2] and Streitwieser[3] have shown that relative acidities of the planar π-electron hydrocarbons are consistent with Hückel MO theory. The differences in acidity were explained by a change of π-electron energy between acids and their respective carbanions. Although there is a good evidence that the acidity of hydrocarbons is considerably influenced by the state of hybridization of the C atom in question,[4] no quantitative correlation has been available hitherto. We examined the acidities of several non-conjugated hydrocarbons and compared theoretical data with experimental ones. Since we are dealing with systems characterized by localized bonds, the scaled maximum overlap method[5, 6] was applied in order to obtain the hybridization parameters. In this procedure the ratio of the s-p content of individual hybrids is varied until the maximum of the suitably scaled bond overlaps is attained. Experimental bond distances and Clementi "double zeta" atomic orbitals[7] were used. During the calculations the bond angles were allowed to follow the directions of hybrids, except in cyclic systems where bent bonds appear. The basic overlap integrals are taken from the tables of Klasinc *et al.*[8] The acidities used were those of the revised McEwen, *et al.* acidity scale.[4] The results are presented in Table 1. The hybrids of the C—H bonds, written in the sp^n form, have generally non-integer exponent* which varies from $n = 1{\cdot}29$ for acetylene to $n = 3{\cdot}00$ for methane. Our results confirm earlier assumptions that the acidity increases with increasing hybrid s-character. The s-orbital, being of lower energy than p-orbital of the same principal quantum number, is more attractive for accommodating the negative charge of the carbanion concerned. The straight line obtained by the least square method may be presented by

$$pK = 83{\cdot}12 - 1{\cdot}33\ (s\%) \qquad (1)$$

* Called also "second order" hybridization[9].

The calculated s-characters do not deviate much from the straight line— standard error is 0·28. When the hybridization is restricted to the idealized or "first order" hybridization, i.e. to the sp, sp^2 and sp^3 hybrids, the deviation is much greater. It has to be pointed out that the difference between "first" and "second order" hybridization is sometimes quite considerable. The striking example is acetylene where we found $sp^{0.77}$ and $sp^{1.29}$ hybrids for C—C and C—H bond respectively.

In conclusion, we may say that hybridization is important for correlating some experimental and calculated quantities. The "second order" hybrids should be taken into account when the acidities of the conjugated hydrocarbons are calculated using HMO method, especially if their geometries differ significantly. A similar precaution is necessary when correlations of other physical quantities, e.g. $J_{C^{13}-C^{13}}$ and $J_{C^{12}-}$ coupling constants versus s-character, are considered.[10]

TABLE 1. HYBRIDS DESCRIBING C—H BONDS OBTAINED BY THE SCALED MAXIMUM OVERLAP METHOD, CORRESPONDING S-PERCENTAGES, THEORETICAL (Eq. 1) AND EXPERIMENTAL ACIDITIES

Molecules	Hybridization	s-character	pK(theoret.)	pK(exp.)[a]
Acetylene	$\psi_{CH} = sp^{1.29}$	43·6%	25·1	25
Propen(2-)	$\psi_{CH} = sp^{2.20}$	31·2%	41·6	40
Ethylene	$\psi_{CH} = sp^{2.17}$	31·6%	41·1	42
Cyclopropane	$\psi_{CH} = sp^{2.40}$	29·4%[b]	44·0	44
Cyclobutane	$\psi_{CH} = sp^{2.74}$	27·6%[b]	46·4	47
Methane	$\psi_{CH} = sp^{3.00}$	25·0%	50·0	47
Cyclopentane	$\psi_{CH} = sp^{2.75}$	26·6%[b]	47·7	48
Ethane	$\psi_{CH} = sp^{2.94}$	25·4%	49·3	48
Propane(2-)	$\psi_{CH} = sp^{2.86}$	25·9%	48·7	49
Cyclohexane	$\psi_{CH} = sp^{2.87}$	25·8%	48·8	49

[a] Experimental pK values are determined with accuracy ± 2.
[b] These hybridization parameters are taken from ref. 6.

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