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# AN LCAO TREATMENT OF THE ACIDITY OF HYDROCARBONS[1]

Andrew Streitwieser, Jr.[2]

Department of Chemistry, University of California

Berkeley, California

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EARLY in the development of the simple molecular orbital theory of organic chemistry, Wheland[3] showed that the theory qualitatively accounts for the acidities of hydrocarbons. The more quantitative experimental pK values of McEwen[4] were not available at that time. It is important to determine the extent to which simple MO theory quantitatively correlates not only McEwen's values but also the acidities of some hydrocarbons of recent interest, for example, the rather acidic fluoradene, I, recently prepared by Rapoport and Smolinsky.[5]

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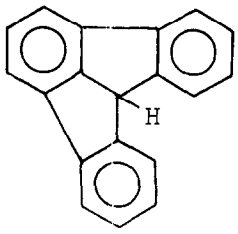
[2] Alfred P. Sloan Fellow; National Science Foundation Science Faculty Fellow, 1959-1960.

[3] G. W. Wheland, J. Chem. Phys. 2, 474 (1934).

[4] W. K. McEwen, J. Am. Chem. Soc. 58, 1124 (1936).

[5] H. Rapoport and G. Smolinsky, ibid. 80, 2910 (1958).

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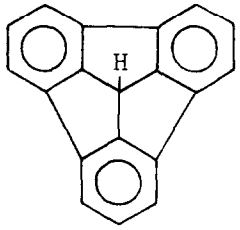


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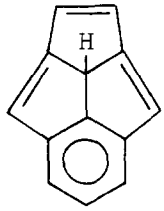


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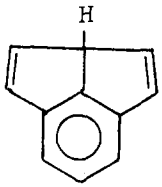


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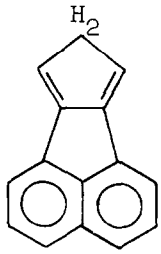


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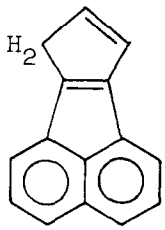


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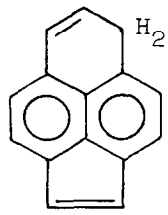


VII

Following Wheland,[3] we assume that the acidity of the hydrocarbon is proportional to the change in the $\pi$-bond energy resulting from the difference in conjugation between the hydrocarbon, $AH_i$, and the corresponding anion, $A_i^-$. We use the usual form of the simple MO theory with neglect of overlap and with all $\beta$'s equal. The $\pi$-energy of a compound with n $\pi$-electrons then takes the form, $E_\pi = n\alpha + M\beta$, in which $\alpha$ is the usual Coulomb integral. Hence:

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

We assume, with Wheland, that effects such as changes in σ-bond energies and solvation are relatively constant from one system to another. Note also that hyperconjugation effects in the hydrocarbon are neglected. We also assume that any strain energy is the same in the hydrocarbon and in the anion.

Wheland assigned a value to β derived from empirical resonance energies. There is reason to suspect this procedure and instead we retain β as an adjustable parameter. The correlation takes the following form, in which the empirical slope, b, contains β:

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

ΔM values and McEwen's pK's for a number of hydrocarbons are summarized in Table I and are plotted in Figure 1. In the scatter of points a good straight line emerges through the three compounds whose anions are expected to be completely coplanar, an assumption implicit in taking all β's equal. The anions of the other compounds contain aryl groups which may be expected to deviate substantially from coplanarity; they are less acidic than predicted by the correlation by about 4 pK units per nonplanar phenyl group, an amount which may be shown to correspond to an angle of twist of roughly 30-40°.

It is unfortunate that the data for planar carbanions is so limited; nevertheless, since the deviations found are in the right direction and are of reasonable magnitude, the correlation should be considered to be successful. Furthermore, we can account very well for the rather more qualitative information

TABLE 1. Acidities of Hydrocarbons

| Compound | ΔM | pK Expl.[a] | pK Calcd. |
|---|---|---|---|
| Indene | 1.747 | 21 | |
| 9-Phenylfluorene | 1.980 | 21 | |
| Fluorene | 1.523 | 25 | |
| Diphenyl-p-biphenylylmethane | 1.819 | 31 | |
| Triphenylmethane | 1.800 | 33 | |
| Diphenylmethane | 1.301 | 35 | |
| Toluene | 0.721 | 37[b] | |
| Cycloheptatriene | 1.110 | >25[c] | 31 |
| Perinaphthene | 1.697 | 16-25[c] | 22 |
| Cyclopentadiene | 2.000 | 16-20[c] | 17 |
| Fluoradene, I | 2.115 | 11,[d] 13.5[e] | 15 |
| Cyclopropene | 0 | | ~48 |
| 1,2,3-Triphenyl-cyclopropene | 1.301 | | 28 |
| 4,5-Methylenephenanthrene | 1.514[f] | | 25 |
| II | 2.225 | | 14 |
| III | 2.189 | | 14.5 |
| IV | 2.411 | | 11 |
| V | 2.024 | | 17 |
| VI | 1.911 | | 18.5 |
| VII | 1.964 | | 18 |

[a] Ref. 4 unless indicated otherwise.
[b] Estimated from cumene.
[c] See text.
[d] In water.
[e] In 97% aqueous methanol.
[f] Experiments with this compound are currently in progress.

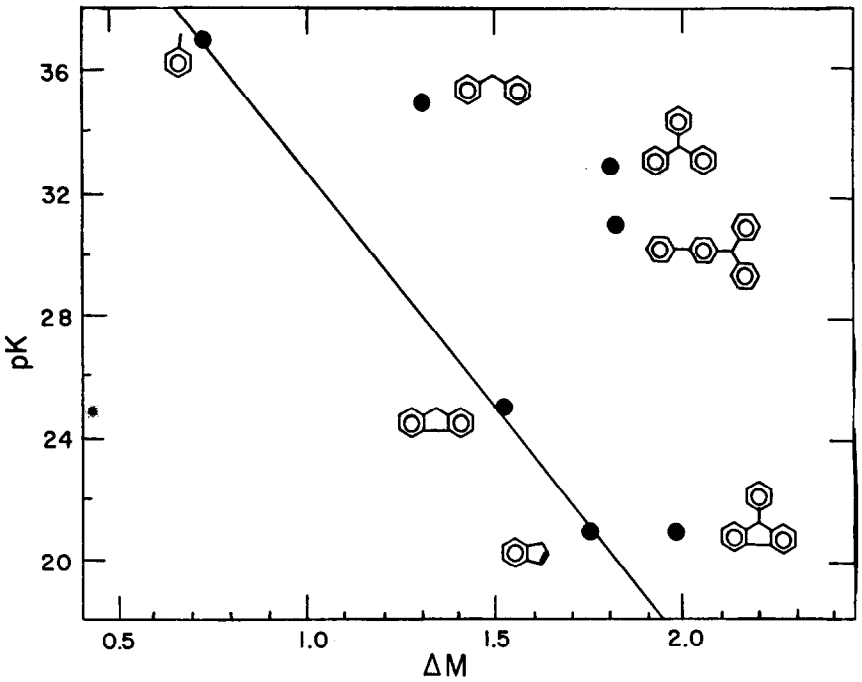


Fig. 1. Correlation of Acidities of Hydrocarbons with Simple MO Calculations

available for several other hydrocarbons. Cycloheptatriene does not condense with ketones or with ethyl oxalate with refluxing alcoholic sodium ethoxide, conditions under which fluorene condenses readily.[6] Hence, cycloheptatriene is less acidic than fluorene in agreement with the calculations. In acidity, perinaphthene apparently lies between cyclopentadiene and fluorene,[7] in agreement with its calculated pK of 22.

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[6] J. Thiele, Ann. 319, 226 (1900); Ber. 33, 851 (1900).

[7] V. Boekelheide and C. E. Larrabee, J. Am. Chem. Soc. 72, 1245 (1950).

Cyclopentadiene reacts with potassium in benzene in the cold, conditions under which indene is inert; cyclopentadienylpotassium is reported to be decomposed by water.[8] Accordingly, the pK of cyclopentadiene probably lies between 16 and 20, in agreement with the calculated value, 17.

The correlation predicts the pK of fluoradene to be 15 in comparison with the experimental value, 11-13.5.[5] Most of McEwen's values are based on experiments in ether or benzene solution but refer to methanol in water, whereas the fluoradene values refer to water and aqueous methanol. The calculated results are not corrected for any effects of solvation. The agreement is good; McEwen's values are not better than $\pm 1$ pK unit.

In Table 1, we predict the acidities of several known and unknown hydrocarbons of theoretical interest. In all of these results, the anion-stabilizing character of the five-membered ring is clearly in evidence. The stability of the cyclopentadienyl anion persists even when this ring system is but a part of a more complex structure. Note, for example, that the introduction of a vinyl bridge in perinaphthene, giving compound VII, results in a calculated decrease of 4 pK units.

Although energies for some of these compounds have been reported previously, in most cases new calculations were made usually with an IBM 701 computer and programs previously

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[8] J. Thiele, Ber. 34, 68 (1901).

discussed.[9] Energies and coefficients for the molecular orbitals and bond orders for many of the compounds described in this paper have been prepared as a separate appendix.[10]

I am indebted to Dr. P. M. Nair, Dr. R. B. Williams, Mr. J. B. Bush and Mr. J. I. Brauman for technical assistance.

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[9] A. Streitwieser, Jr. and P. M. Nair, Tetrahedron 5, 149 (1959).

[10] Material supplementary to this article has been deposited as Document number 6229 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C. A copy may be secured by citing the Document number and by remitting $2.50 for photoprints, or $1.75 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.