Acidity of Hydrocarbons. XXII. Relative Equilibrium Acidities of Hydrocarbons toward Cesium Cyclohexylamide[1]

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Abstract: Relative equilibrium acidities are determined for nine of the hydrocarbons in the preceding paper plus five others toward cesium cyclohexylamide (CsCHA) in cyclohexylamine. CsCHA is an effectively stronger base toward these hydrocarbons than is LiCHA, but relative equilibrium acidities are much the same. Relative to 9-phenylfluorene, whose p*K* is taken as 18.49, the following p*K* values are derived: 3,4-benzfluorene, 19.45; indene, 19.93; 1,2-benzfluorene, 20.05; benzanthrene, 21.17; 4,5-methylenephenanthrene, 22.63; fluorene, 22.74; 2,3-benzfluorene, 23.17; 1,1,3-triphenylpropene, 26.59; 10-phenyl-9,9-dimethyldihydroanthracene, 28.04; 9-phenylxanthene, 28.5; *p*-biphenylyldiphenylmethane, 30.20; triphenylmethane, 31.48; diphenylmethane, 33.1. These values for the hydrocarbons expected to give planar carbanions are found to give poor correlations with simple MO theory. Other implications of these data are discussed.

During the course of extensive studies on kinetics of exchange of hydrocarbons with lithium cyclohexylamide, we found that the use of cesium cyclohexylamide gave faster exchange by several orders of magnitude.[2] The use of the latter catalyst has allowed a convenient extension of measurements of exchange rates to hydrocarbons of rather low acidity. This effect of the metal cation on exchange rates can be rationalized in a straightforward way. More surprising is the observation that a similar effect is encountered in equilibrium acidities of hydrocarbons in cyclohexylamine.

In the preceding paper[1b] we reported equilibrium constants for reaction 1. This technique was applicable

$$\mathrm{RH + R'Li \rightleftharpoons RLi + R'H} \qquad (1)$$

to hydrocarbons of the order of acidity of fluorene but could not be applied to compounds as weakly acidic as triphenylmethanes. Triphenylmethyllithium does not obey Beer's law in cyclohexylamine;[3] that is, reaction 2 does not lie all the way to the right. We found, however, that triphenylmethylcesium does obey Beer's law[4]—triphenylmethane is a stronger acid toward cesium cyclohexylamide (CsCHA) than it is toward lithium cyclohexylamide (LiCHA). Thus, we undertook a study of equilibria 3 for extension to weaker hydrocarbon acids. It further developed that these

$$\mathrm{RH + LiNHC_6H_{11} \rightleftharpoons RLi + C_6H_{11}NH_2} \qquad (2)$$

$$\mathrm{RH + R'Cs \rightleftharpoons RCs + R'H} \qquad (3)$$

solutions were more stable than those of the lithium salts; hence, we studied equilibria 3 as well for the same series of hydrocarbons previously measured toward lithium. In this paper we present these equilibrium constants and compare them with the comparable lithium values as well as with other experimental and theoretical measures of hydrocarbon acidity.

Experimental Section

Materials Used. Most of the hydrocarbons used have been described previously.[1b] Triphenylmethane and diphenylmethane were commercial materials. *p*-Biphenylyldiphenylmethane[5] was prepared by hydrogenolysis over Pd–C of the carbinol prepared from benzophenone and *p*-biphenylyllithium; mp 113.5–114.5° (lit.[6] mp 111–112°).

Procedure. Cesium metal was prepared by pyrolysis of cesium azide;[2] the triply distilled material was allowed to react with cyclohexylamine to make the stock solution of CsCHA. Spectra were taken in the apparatus described previously[1b] and the same general procedure was followed except that the carbanions were generated by injection of CsCHA stock solution using a Hamilton gas-tight syringe. The standard spectra were taken in the same way except that excess CsCHA was used. Spectra of the cesium salts not previously reported[2,4] are given in Table I. The equilibrium constants measured are summarized in Table II. In this table the more acidic hydrocarbon is listed first and the entries have their previous significance.[1b]

Table I. Spectra of Cesium Salts of Hydrocarbons in Cyclohexylamine

Anion	$\lambda_{\max}$, mμ (ϵ)
9-Phenylfluorenyl	398 (~22,300), 456 (1738), 484 (2145), 516 (1677)
Indenyl	372 (1140)
Benz[*a*]fluorenyl	426 (8780)
Benzanthracyl	448 (37,200)
Benz[*c*]fluorenyl[a]	394 (5070), 483 (2720), 514 (2250)
α,α,γ-Triphenylallyl	470 (23,500), 551 (46,500)

[a] Replaces earlier report (ref 4).

Results and Discussion

Experimental Errors. The same general errors are present in this study as in the preceding study using lithium salts.[1b] The solutions usually decayed slowly with time, presumably because of reaction with traces of dissolved oxygen and perhaps also with stopcock grease. The cesium salt solutions were generally more stable than the comparable lithium solutions, and the present results are probably both more precise and more accurate. The replicate experiments often gave agreement to better than 10%, although in some cases the reproducibility was considerably less. On taking

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(1) (a) Supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Grants No. 62-175 and 64-554; (b) paper XXI: A. Streitwieser, Jr., J. H. Hammons, E. Ciuffarin, and J. I. Brauman, *J. Am. Chem. Soc.*, **89**, 59, (1967).

(2) A. Streitwieser, Jr., and R. A. Caldwell, *ibid.*, **87**, 5394 (1965).

(3) A. Streitwieser, Jr., and J. I. Brauman, *ibid.*, **85**, 2633 (1963).

(4) A. Streitwieser, Jr., J. I. Braumann, J. H. Hammons, and A. H. Pudjaatmaka, *ibid.*, **87**, 384 (1965).

(5) Preparation by M. R. Granger.

(6) H. Gilman and H. L. Jones, *J. Am. Chem. Soc.*, **51**, 2840 (1929).

Table II. Relative Equilibria of Hydrocarbons toward CsCHA

RH			R'H				
Symbol^a	$[RH]_0$, 10^4 M	[RCs], 10^4 M	Symbol^a	$[R'H]_0$, 10^4 M	[R'Cs], 10^4 M	K^b	n^f
9-PF	47.3	5.46	1,2-BF	278	0.966	36.4^c	1
3,4-BF	22.5	2.04	1,2-BF	7.46	0.162	4.5	1
	23.9	2.20		15.5	0.402	3.85 ± 0.15^c	3
In	169.8	10.4	1,2-BF	14.2	0.70	1.27^c	1
	106.8	9.02		11.7	0.74	1.37^c	1
3,4-BF	14.69	2.03	BA	27.9	0.091	48.4 ± 0.3^c	2
	11.27	1.78		38.1	0.149	47.5 ± 0.7^c	2
In	130.2	9.36	BA	27.0	0.112	19.1 ± 1.0^c	5
3,4-BF	5.87	2.09	4,5-MP	1660	0.602	1524 ± 40^c	9
4,5-MP	73.0	6.61	F	361	25.7	1.30 ± 0.15^d	10
4,5-MP	32.1	1.29	2,3-BF	32.1	0.378	3.48 ± 0.3^c	8
2,3-BF	0.833	0.457	TriPP	251	0.120	2300± 600^c	5
	7.11	3.23		461	0.141	2750 ± 90^c	4
TriPP	0.743	0.0333	PDDA	202	0.269	35.2^c	1
	4.72	0.132		1207	0.459	27.2 ± 0.5^c	4
PDDA	7.95	0.327	9-PX	7.10	0.955	3.02 ± 0.4^d	9
PDDA	0.447	0.113	BDPM	105	0.214	165 ± 12^d	19
	1.34	0.244		332	0.235	124 ± 6^d	10
9-PX	0.545	0.0792	BDPM	83.3	0.117	~130^{d,e}	20
BDPM	2.08	0.271	TriPM	13.5	0.911	21.7 ± 1.5^d	5
	1.78	0.079		26.4	0.756	16.2 ± 1.0^d	12
TriPM	3.61	0.197	DiPM	139	0.160	51 ± 36^d	26
	16.3	0.298		279	0.157	33.0 ± 3.1^d	18

[a] Defined in Table IV. [b] $K = [RCs]([R'H]_0 - [R'Cs])/([RCs]([RH]_0 - [RCs]))$. [c] By E. C. [d] By J. H. H. [e] Large error. [f] Number of scans during run. A small number of scans indicates a more slowly decomposing solution.

Table III. Summary of Alkylcesium Equilibrium Constants

RH^a	R'H^a	K	log K	log K for lithium^b
3,4-BF	1,2-BF	4.0 ± 0.03	0.60 ± 0.03	0.59 ± 0.02
4,5-MP	2,3-BF	3.5 ± 0.3	0.58 ± 0.04	0.56 ± 0.02
4,5-MP	F	1.30 ± 0.2	0.11 ± 0.06	0.23 ± 0.03
2,3-BF	TriPP	2650 ± 150^c	3.42 ± 0.03	3.26 ± 0.15
9-PF	1,2-BF	36.4	1.56 ± 0.01	1.48 ± 0.03
3,4-BF	4,5-MP	1524 ± 40	3.18 ± 0.02	3.15 ± 0.03
3,4-BF	BA	48 ± 1	1.68 ± 0.01	1.19 ± 0.01
In	1,2-BF	1.32 ± 0.05	0.12 ± 0.02	−0.27 ± 0.02
In	BA	19 ± 1	1.28 ± 0.02	0.53 ± 0.02
TriPP	PDDA	28 ± 2	1.45 ± 0.03	
PDDA	9-PX	3.0 ± 0.4	0.48 ± 0.06	
PDDA	BDPM	145 ± 20	2.16 ± 0.06	
9-PX	BDPM	~130	~2.1	
BDPM	TriPM	19 ± 3	1.28 ± 0.07	
TriPM	DiPM	38 ± 5^c	1.6 ± 0.1	

[a] Chemical abbreviations are defined in Table IV. [b] From ref 1b. [c] Weighted average.

logarithms, these uncertainties are compared with the total range of values and are acceptably small.

Average values for equilibrium pairs are summarized in Table III together with a comparison of lithium results from the preceding paper.[1b] With some notable exceptions the cesium and lithium systems give similar numbers. Indene (In) is relatively substantially more acidic toward CsCHA than toward LiCHA, whereas benzanthrene (BA) shows the reverse tendency. These differences may reflect a difference in the ion pairs involved (*vide infra*). The many similarities that are evident probably demonstrate the reproducibility and accuracy of the numbers. The uncertainties assigned to the equilibrium constants appear to be realistic as probable errors.

Acidity Order. From the average equilibrium constants for pairs of hydrocarbons, the sequential order of relative acidities in Table IV can be derived. Except for In and BA, the agreement between the Cs and Li relative equilibrium constants is excellent. This agreement suggests that the assigned probable errors are reasonable and that the differences found for In and BA are real.

These lists of equilibrium constants have obvious value as measures of hydrocarbon acidities, but such application assumes that the alkylcesium ion pairs are valid models for carbanions and that the same type of ion pair is involved for each compound. The latter assumption is probably reasonable. In their work with fluorenyl ion pairs in ether, Hogen-Esch and Smid[7] found that the cesium salt was present generally as contact ion pairs whereas the lithium salt often existed at least partially as solvent-separated ion pairs. They argue that the large cesium cation is not solvated specifically and is satisfied as the contact ion pair with a large and diffuse anion, whereas the small lithium cation prefers the solvation of several Lewis base solvent molecules to close association with the anion. The argument finds support in recent studies of the propagation step in anionic polymerization.[8,9] The same type of explanation may well be applicable in cyclohexylamine. The entropy of activation for exchange of toluene-α-*d* with LiCHA suggests that the lithium cation has additional solvation at the transition state;[10] no such additional solvation is evident in exchange reactions with CsCHA.[2] The aggregation of LiCHA in cyclohexylamine undoubtedly reflects the same need for solvation.[10,11] This evidence is suggestive that the

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(7) T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **87**, 669 (1965); **88**, 307, 318 (1966).

(8) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965).

(9) D. N. Bhattacharyya, J. Smid, and M. Szwarc, *ibid.*, **69**, 624 (1965).

(10) A. Streitwieser, Jr., R. A. Caldwell, M. R. Granger, and P. M. Laughton, *ibid.*, **68**, 2916 (1964).

(11) A. Streitwieser, Jr., D. E. Van Sickle, and W. C. Langworthy, *J. Am. Chem. Soc.*, **84**, 244 (1962).

Table IV. Acidity Order of Hydrocarbons

Hydrocarbon		Rel −log *K* toward CsCHA	Rel −log *K* toward LiCHA	p*K* CsCHA	DMSO systems[a]	McEwen[b]
Name	Symbol					
9-Phenylfluorene	9-PF	0	0	(18.49)[c]	18.38, 18.59[d]	21
3,4-Benzfluorene	3,4-BF	0.96 ± 0.03	0.89 ± 0.04	19.45		
Indene	In	1.44 ± 0.02	1.75 ± 0.04	19.93	18.2	
1,2-Benzfluorene	1,2-BF	1.56 ± 0.01	1.48 ± 0.03	20.05		
Benzanthrene	BA	2.64 ± 0.04 2.72 ± 0.03	2.18 ± 0.07	21.17		
4,5-Methylenephenanthrene	4,5-MP	4.14 ± 0.04	4.11 ± 0.06	22.63		
Fluorene	F	4.45 ± 0.07	4.34 ± 0.07	22.74	20.5	25
2,3-Benzfluorene	2,3-BF	4.68 ± 0.06	4.67 ± 0.07	23.17		
1,1,3,3-Tetraphenylpropene	TetraPP		7.7 ± 0.2			
1,1,3-Triphenylpropene	TriPP	8.10 ± 0.07	7.9 ± 0.2	26.59		
10-Phenyl-9,9-dimethyldihydroanthracene	PDDA	9.55 ± 0.08		29.04		
9-Phenylxanthene	9-PX	10.0		28.5	24.2	
p-Biphenylyldiphenylmethane	BDPM	11.71 ± 0.10		30.20	45.3	31
Triphenylmethane	TriPM	12.99 ± 0.33		31.48	27.2	33
Diphenylmethane	DiPM	14.6 ± 0.14		33.1	28.6	55

[a] Reference 16 except where noted; based on *p*-nitroaniline as a standard with p*K* = 18.4. [b] Reference 15. [c] Reference 13. [d] Reference 14.

equilibria with cyclohexylamine of hydrocarbons whose conjugate bases are delocalized carbanions should be represented as

$$RH + Li^{+}\,^{-}NHC_6H_{11} \rightleftharpoons R^{-}||Li^{+} + C_6H_{11}NH_2 \quad (4)$$

$$RH + Cs^{+}\,^{-}NHC_6H_{11} \rightleftharpoons R^{-}Cs^{+} + C_6H_{11}NH_2 \quad (5)$$

in which the symbol || denotes solvent separation. In (5) only contact ion pairs are involved whereas in (4) the equilibrium involves a solvent-separated lithium carbanide salt competing with a contact ion pair LiCHA salt. The larger charge separation involved in (4) provides an easy rationalization for the effectively lower acidity of hydrocarbons toward LiCHA than toward CsCHA. Clearly, the effect of temperature on the spectra of these salts in CHA would be helpful; such experiments are in progress.

A corollary is that a carbanion with a more concentrated charge should have a relatively greater equilibrium acidity toward CsCHA than toward LiCHA because a smaller increase in charge separation is involved for the Cs salt. Let us assume for the carbanions studied here that the cation lies above the central ring and that, to a first approximation, the electrostatic attraction is determined primarily by the charge density of this central ring. The cyclopentadienyl ring in the In anion has a total HMO π-electron charge density of 0.76 whereas that in the fluorenyl and benzfluorenyl anions is 0.61–0.67.[12] The central six-membered ring in BA anion has a total charge of only 0.32.[12] Recall that the fluorenes have the same relative acidities toward LiCHA and CsCHA, indene is a stronger acid toward CsCHA, and BA is a stronger acid toward LiCHA. There appears to be a real trend that, the more concentrated the charge near the cation, the more stable the anion is when associated with cesium cation. This generalization extends to the di- and triarylmethanes. In triphenylmethyl anion, for example, the charge is located principally on the central carbon and on the *ortho* positions and, as previously mentioned, triPM is substantially more acidic toward CsCHA than toward LiCHA. This difference in ion-pair character may also be the reason that the lithium salts appear to decompose in cyclohexylamine more rapidly than the cesium salts.[1b]

The several differences between the lithium and cesium salts also point up the dangers inherent in assuming a universally applicable p*K* scale for hydrocarbons. The relative log *K* values in Table IV correspond to p*K* differences if the cesium carbanide ion pairs are treated as free carbanions. In order to convert them to more common units, they have been converted to absolute p*K*'s using the value of 18.49 for 9-PF obtained by Langford and Burwell[13] in aqueous sulfolane. The determinations of Bowden and Stewart[14] give the same average—18.38 in aqueous dimethyl sulfoxide, 18.59 in ethanolic dimethyl sulfoxide. The absolute p*K* values so derived certainly have far less significance than the differences between two such numbers. The numbers given in Table IV differ from those which we reported previously[4] in being based entirely on equilibria with CsCHA rather than LiCHA. The differences are minor except for PDDA and the hydrocarbons of lower acidity which are now assigned p*K* values about 1 unit lower than the earlier report. The lithium equilibrium which related PDDA to triPP and the more acidic hydrocarbons was found to be particularly poor;[1b] the present cesium values should be far more accurate.

In Table IV we compare these results with the p*K*'s of McEwen,[15] which were highly approximate values based on organometallic ion pairs and which for several decades were the only p*K*'s available for hydrocarbons. We find that the present alkylcesium equilibria give p*K*'s averaging about 2 units lower than McEwen's values, but that otherwise the correspondence is amazingly good.

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(12) A. Streitwieser, Jr., and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Pergamon Press, New York, N. Y., 1965.

(13) C. H. Langford and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **82**, 1503 (1960).

(14) K. Bowden and R. Stewart, *Tetrahedron*, **21**, 261 (1965).

(15) W. K. McEwen, *J. Am. Chem. Soc.*, **58**, 1124 (1936).

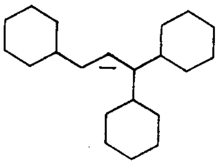
Steiner and Gilbert[16] have recently communicated the pK's by the H_- technique in dimethyl sulfoxide media of several of the same hydrocarbons studied in the present work. Their values are also given in Table IV. The agreement with the present work was poor, but many of the DMSO values were assigned tentatively and are being changed by more recent measurements to accord more closely with ours; in particular, pK's of hydrocarbons less acidic than fluorene are being increased by 1.6 units.[16b] It is premature to discuss the differences at this point, and further comment is deferred to the completion of the Steiner and Gilbert studies. Note, for example, that the Steiner–Gilbert pK's are based on *p*-nitroaniline as the anchor compound, whereas we use 9-PF.

Structure and Acidity. The present data allow a more quantitative discussion of the effect of several structural factors on acidity. Toluene is of the order of 5–8 pK units more acidic than methane;[17] our present estimate of the pK of toluene is about 40. Thus, putting a second benzene ring on methane (pK of diphenylmethane = 33) has about the same acidifying effect as the first. The third phenyl group in triphenylmethane has a further acid-strengthening effect of hardly more than 1 pK unit. Most, if not all, of this further increment is undoubtedly associated with the inductive effect of the phenyl group since this effect is known to be important in these carbanions.[18,19] Consequently, the third phenyl group provides little, if any, additional net conjugation compared to the diphenylmethyl anion, unquestionably because the rings are seriously twisted from coplanarity.

The situation with carbonium ions presents a significant contrast. Comparing the pseudo-basicity of carbinols—the equilibrium with carbonium ions—the change from benzyl alcohol to benzhydrol causes an increase in pseudo-basicity of 9–14 powers of ten, whereas the addition of a third benzene ring gives a further increase in pseudo-basicity of almost 7 powers of ten. Perhaps it is more important for a carbonium ion to distribute electron deficiency in a π system than it is for a carbanion to so distribute excess negative charge, again because of the significant electron-attracting inductive effect of benzene rings. If so, the benzene rings in triphenylmethyl anion would be more twisted from coplanarity than those in triphenylmethyl cation. It should be noted that our triphenylmethyl anion has the further perturbation of a cesium cation probably sited near the central carbon; however, ΔpK for diPM and triPM in DMSO, in which the free carbanions are probably involved, is 1.4,[16] close to our value of 1.6. It should be noted further that this apparent difference between carbonium ions and carbanions for alternant systems does not appear in even relatively sophisticated MO theories of the Pariser–Parr–Pople type, but neither do these MO methods account adequately for the inductive effect of π carbons.

The relative impotence of too many phenyls appears also in the comparison of the pK's of 1,1,3-triphenylpropene (triPP) and 1,1,3,3-tetraphenylpropene (tetraPP), the statistically corrected values for which are, respectively, 26.7 and 25.9. In the anions, shown respectively as I and II, the steric interference of two bottom phenyls prevents full conjugation. Note by comparison that a phenyl substituent in the *para* position of triPM has a larger acid-strengthening effect.

Using an oxygen to bridge two phenyl rings in triphenylmethyl anion giving the 9-phenylxanthyl anion III causes an increase in acidity by 3 pK units even though a conjugated oxygen generally diminishes acidity.[20] This effect undoubtedly arises largely from the coplanarity of the two rings resulting from removal of *o*-hydrogen repulsions, although an additional entropy effect is not insignificant. In triPM, the benzene rings have some freedom to rotate about the single bonds to the central carbon. Such rotation is frozen in the anion because of the need to maintain conjugation. Consequently, removing the proton from an acyclic C–H is associated with a decrease in entropy that is not shared by cyclic C–H groups in which such rotations are also restricted in the hydrocarbon. It is difficult to estimate the magnitude of this rotational entropy effect, particularly in compounds such as the triarylmethanes in which the rings have some restriction of movement, but it could amount to a factor of 2–5 in K or an increase of 0.3–0.7 in pK.[21]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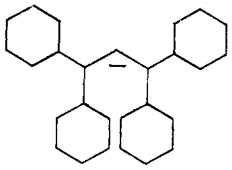
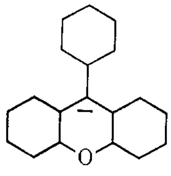

II

Similar effects appear in the acidity of PDDA whose anion is IV. This hydrocarbon is substantially more acidic than triPM because of increased coplanarity in IV and the rotational entropy effect cited above, and probably also because of some relief of steric strain between the tertiary hydrogen and *gem*-dimethyl groups in PDDA, despite the acid-weakening inductive effect of the *o*-alkyl substituents.[22]



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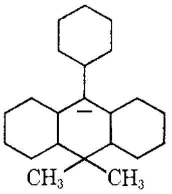

IV

From these results we estimate the pK of triPM to a hypothetical ion with two strain-free coplanar rings to be somewhat greater than 27.5. Thus, we estimate that, of the 13 pK units by which 9-PF is more acidic than triPM, <4 units is associated with the planarity of the fluorene ring and >9 units is associated with the unique anion-stabilizing properties of the cyclopentadienyl ring system.

Molecular Orbital Theory. Several of the hydrocarbons studied in the present work have planar anions and are well suited to examination by molecular orbital

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(16) (a) E. C. Steiner and J. M. Gilbert, *J. Am. Chem. Soc.*, **87**, 383 (1965); (b) personal communication from Dr. E. C. Steiner.

(17) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965.

(18) A. Streitwieser, Jr., R. A. Caldwell, and M. R. Granger, *J. Am. Chem. Soc.*, **86**, 3578 (1964).

(19) A. Streitwieser, Jr., and R. G. Lawler, *ibid.*, **87**, 5388 (1965).

(20) A. Streitwieser, Jr., and H. F. Koch, *ibid.*, **86**, 404 (1964).

(21) We are indebted to Dr. G. Haefelinger for initial suggestions of this effect.

(22) Unpublished experiments of Dr. G. Haefelinger.

theories. Wheland[23] suggested that an important factor in acidities of many hydrocarbons is the increase in π conjugation in the change from hydrocarbon to carbanion, and he showed that the qualitative data available at that time agreed with a simple molecular orbital model. In this model, HMO calculations of the π-electron system of the hydrocarbon, $E_\pi = n\alpha + M\beta$, and of the carbanion, $E_\pi^- = (n + 2)\alpha + M^-\beta$, give the π-energy change, $\Delta E_\pi = 2\alpha + \Delta M\beta$.[24] This method has been shown to account satisfactorily for the pK values of McEwen.[25]

In Table V we list those HMO quantities for the hydrocarbons whose conjugate bases are expected to be planar. The cesium relative pK values of these hydrocarbons are plotted against the corresponding ΔM values in Figure 1. The correlation is extremely poor. There is a trend toward higher acidity for higher ΔM, as expected, but the wide scatter makes such a plot useless for predictive purposes.

Table V. HMO Quantities for Planar Carbanions

Hydrocarbon	M^a	M^{-a}	ΔM	q_r^a	$-\log K_{\mathrm{rel}}$ (cesium), cor^b
3,4-BF	22.084	23.664	1.580	1.284	1.26
In	10.424	12.171	1.746	1.252	1.44
1,2-BF	22.069	23.679	1.610	1.271	1.86
BA	22.084	23.582	1.497	1.326	2.98
4,5-MP	19.448	20.962	1.514	1.326	4.44
F	16.383	17.906	1.523	1.322	4.55
2,3-BF	23.069	23.553	1.484	1.338	4.98

[a] The quantities were largely taken from ref 12. [b] Relative acidity per hydrogen: 9-PF = 0.

We expect that, as the negative charge on the central carbon increases, the carbanion would tend to react more readily with solvent and the acidity would diminish. Table V also lists the HMO electron densities, q_r, for the central carbon of the planar carbanions.

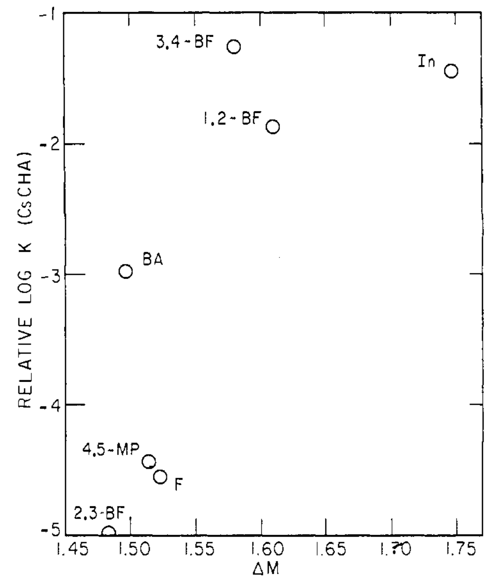

Figure 1. Correlation of hydrocarbon acidities with ΔM values of simple MO theory.

A plot of these quantities against the relative acidities also shows a general trend in the expected direction, but again the quantitative correlation is poor. The lack of success may result from the present use of a free carbanion as the model for the experimental ion pairs or from limitations inherent in the HMO approximations. For the latter, the trouble may well lie in the neglect of electron repulsion terms characteristic of the HMO method. Dewar and Thompson[26] have already shown that the LiCHA-catalyzed exchange rates of deuteriomethylarenes[27] are correlated better by SCF methods than by the HMO method,[28] but some limitations of the present SCF methods have been noted above. We are presently studying the further application of such advanced MO methods to the present data and are extending the present experimental techniques to other systems of interest.

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