

$$\frac{{}^s K_1' {}^s K_2'}{{}^s K_2' {}^s K_3'} \cdots \frac{{}^s K_{n-1}'}{{}^s K_n'} = \frac{K_1 {}^s \Gamma_2}{K_2 {}^s \Gamma_1} \cdots \frac{K_{n-1} {}^s \Gamma_n}{K_n {}^s \Gamma_{n-1}} = \frac{K_1 {}^s \Gamma_n}{K_n {}^s \Gamma_1}$$

for a constant solvent system and

$$\frac{{}^1 K_1' {}^2 K_2'}{{}^1 K_2' {}^2 K_3'} \cdots \frac{{}^s K_{n-1}'}{{}^s K_n'} = \frac{K_1 {}^1 \Gamma_2}{K_2 {}^1 \Gamma_1} \cdots \frac{K_{n-1} {}^s \Gamma_n}{K_n {}^s \Gamma_{n-1}} = \frac{K_1 {}^s \Gamma_n {}^1 \Gamma_2}{K_n {}^1 \Gamma_1 {}^2 \Gamma_2} \cdots \frac{{}^{s-1} \Gamma_{n-1}}{{}^s \Gamma_{n-1}}$$

for a changing solvent system, where K_n = thermodynamic ionization constant of indicator n , ${}^2 K_n'$ = concentration ionization constant of indicator n in solvent 2, and ${}^s \Gamma_n$ = activity coefficient ratio for indicator n in solvent s (DMSO). In order for the same relative acidity to be obtained in the two types of solvent systems, it is necessary that

$$\frac{{}^s \Gamma_n}{{}^s \Gamma_1} = \frac{{}^s \Gamma_n {}^1 \Gamma_2 {}^2 \Gamma_3}{{}^1 \Gamma_1 {}^2 \Gamma_2 {}^3 \Gamma_3} \cdots \frac{{}^{s-1} \Gamma_{n-1}}{{}^s \Gamma_{n-1}}$$

It seems very improbable that this relationship would hold if the individual ratios changed markedly, and this suggests that the ratios are nearly constant and equal to unity by definition. This in turn suggests that an H^- scale based on the indicators will be valid in these solvents of high dielectric constants.

Although the indicators appear to behave ideally in these solvents, it is unlikely that this will be generally true. Due to the highly delocalized charge on the indicator anions and the high dielectric constant of the solvents, the salts are probably highly dissociated.^{8,9} There should also be a minimum of difference in specific solvation effects on the anion and neutral molecule. In solvents of low dielectric constant, ion pairing is important and could cause large deviations from ideality. This effect probably accounts for the different relative acidities found by Streitwieser, *et al.*,¹⁰ for some of the indicators studied here.

(8) K. Ziegler and H. Wollschitt, *Ann.* **479**, 123 (1930).

(9) Preliminary conductivity measurements made in this laboratory by Dr. G. J. McDonald support this statement.

(10) A. Streitwieser, Jr., J. I. Brauman, J. H. Hammons, and A. H. Pudjaatmaka, *J. Am. Chem. Soc.*, **87**, 384 (1965).

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Equilibrium Acidities of Hydrocarbon Acids in Cyclohexylamine¹

Sir:

The importance of acidity measurements on proton acids in the elucidation of molecular properties has long been recognized. Nevertheless, experimental work on equilibrium acidities of hydrocarbon acids too weak to be studied in hydroxylic solvents (*i.e.*, pK 's greater than about 20) has been almost nonexistent. In the 1930's, Conant and Wheland² and McEwen³ made semi-

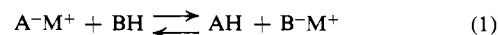
(1) Acidity of Hydrocarbons. XVI. Part XV: A. Streitwieser, Jr., R. A. Caldwell, and M. R. Granger, *J. Am. Chem. Soc.*, **86**, 3578 (1964). This research was supported in part by grants from the Air Force Office of Scientific Research and the Petroleum Research Fund of the American Chemical Society.

(2) J. B. Conant and G. W. Wheland, *ibid.*, **54**, 1212 (1932).

(3) W. K. McEwen, *ibid.*, **58**, 1124 (1936).

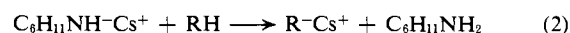
quantitative determinations of pK 's of some hydrocarbon acids, but no other quantitative work in this area has been reported. We report herein the results of more precise equilibrium acidity measurements in the pK range 18–34.

Equilibrium constants were determined in cyclohexylamine for reactions (1) in which AH and BH are



hydrocarbons whose corresponding carbanions show usable spectral differences and M is lithium or cesium. The solutions were made up on a vacuum line with careful exclusion of air and moisture using known amounts of hydrocarbons and solvent and amounts of lithium cyclohexylamide or cesium cyclohexylamide such that measurable amounts of all four components were present. The concentrations of the two anions at equilibrium were determined from visible spectra of the solutions and the spectral data of Streitwieser and Brauman⁴ plus the additional results in Table I.

The organocesium compounds studied obeyed Beer's law over a concentration range of at least 10-fold, showing that reaction 2 goes to completion. The



lithium salts of all compounds more acidic than *p*-biphenyldiphenylmethane also obeyed Beer's law, but Beer's law correlations could not be obtained for solutions of *p*-biphenyldiphenylmethane, triphenylmethane, or diphenylmethane in lithium cyclohexylamide-cyclohexylamine. These compounds are clearly not much more acidic than cyclohexylamine and are not completely converted to the lithium salts. It is clear from the differences between the cesium and lithium salts of these hydrocarbons that the acidity of cyclohexylamine relative to hydrocarbons depends on the metal used. This result is undoubtedly a manifestation of the concentrated charge in cyclohexylamide ion compared to the charge delocalization in the carbanion.

The absorbances of the equilibrium solutions decreased slowly with time, presumably from reaction of base with water in the glass or with the silicone stopcock grease, but the calculated equilibrium constant for any pair of hydrocarbons did not vary significantly over the observed range of anion concentrations. Our procedure establishes relative equilibrium acidities; however, it is convenient to record the results as absolute pK values. This was done by arbitrary reference to 9-phenylfluorene, which Langford and Burwell⁵ found to have $pK = 18.5 \pm 0.1$ in aqueous sulfolane. The results are summarized in Table II. Although we plan to extend the present methods to additional hydrocarbons of interest and to provide cross-checks within the present series, most of the important equilibria in Table II have been reproduced by two independent workers⁶ and we do not expect the present numbers to change by more than ~ 0.2 pK unit.

One of the important aspects of the present results is their confirmation of McEwen's approximate assignments. Our earlier suggestion⁷ that the McEwen scale

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

(5) C. H. Langford and R. L. Burwell, Jr., *ibid.*, **82**, 1503 (1960).

(6) Unpublished results of Dr. E. Ciuffarin.

(7) A. Streitwieser, Jr., W. C. Langworthy, and J. I. Brauman, *J. Am. Chem. Soc.*, **85**, 1761 (1963).

Table I. Absorption of Anions

Anion	Cation	λ_{\max} , m μ (ϵ)		
Fluorenyl	Li	452 (1080),	477 (1300),	510 (827)
	Cs	447 (984),	472 (1200),	504 (870)
1,2-Benzofluorenyl	Li	425 (8140)		
	Li	420 (22,000),	605 (1710),	657 (1290)
2,3-Benzofluorenyl	Cs	418 (19,300),	599 (1560),	648 (1230)
	Li	397 (4800),	465 (2060),	487 (2,600), 519 (2,040)
3,4-Benzofluorenyl	Li		455 (2140),	477 (2430), 508 (1,950)
	Li	452 (1950),	487 (2280),	520 (1690)
9-Phenylfluorenyl	Li	505 (7360)		
4,5-Methylenephenanthrenyl	Cs	505 (6850)		
	Li	470 (21,400),	556 (46,200)	
1,3,3-Triphenylpropenyl	Li	454 (31,500)		
	Cs	445 (33,600)		
9,10-Dihydro-9,9-dimethyl-10-phenyl-anthracenyl	Li	587 ^a		
	Cs	573 (44,300)		
<i>p</i> -Biphenyldiphenylmethyl	Li	488 ^a		
	Cs	488 (28,500)		
Triphenylmethyl	Li	443 ^a		
	Cs	443 (37,200)		

^a No extinction coefficient calculated, as the anion does not obey Beer's law with lithium.

Table II

Compound	pK		Rel. ex- change rates ^c
	This work ^a	McEwen ^b	
9-Phenylfluorene	(18.5) ^d	21	47
3,4-Benzofluorene	19.4		26.3
1,2-Benzofluorene	20.0		7.6
4,5-Methylenephenanthrene	22.6		1.93
Fluorene	22.9	25	1
2,3-Benzofluorene	23.2		0.60
1,1,3-Triphenylpropene	26.5		
9,9-Dimethyl-10-phenyldihydro-anthracene	29.0 ^e		
<i>p</i> -Biphenyldiphenylmethane	31.2 ^e	31	
Triphenylmethane	32.5 ^e	33	
Diphenylmethane	34.1 ^e	55	

^a Estimated relative precision = ± 0.2 pK unit. ^b Ref. 3. McEwen's values are relative to methanol, pK = 16. ^c Hydrogen-tritium exchange rates with sodium methoxide in methanol at 44.9°. ^d Ref. 5. ^e Equilibrium experiments between two compounds of pK's 29 and greater were done with cesium cyclohexylamide. All others were done with lithium cyclohexylamide.

is seriously compressed is clearly not sustained by these experiments; the deficiencies in the molecular orbital argument which led to this suggestion are currently under study. The concurrent work of Steiner and Gilbert⁸ also gives qualitatively comparable pK values for the hydrocarbons in dimethyl sulfoxide-methanol mixtures, although there are serious quantitative differences from our values. The difference in solvent system may be responsible since our equilibria involve ion pairs and those of Steiner and Gilbert undoubtedly involve largely the dissociated ions. If this interpretation is correct, applications of these pK scales will require cognizance of the ionic state.

It has long been known that closure of the *ortho* positions in diphenylmethanes to give fluorenes results in an increase in acidity but it has not been clear how much of this effect results from the increased coplanarity of the benzene rings in this process and how much is associated with the cyclopentadienyl anion ring system.

(8) E. C. Steiner and J. M. Gilbert, *J. Am. Chem. Soc.*, **87**, 382 (1965).

In this regard it is pertinent that 9,9-dimethyl-10-phenyldihydroanthracene, which may be thought of as a triphenylmethane in which two of the phenyl rings are forced to be more nearly coplanar, is a stronger acid than triphenylmethane by 3.5 pK units; the in-

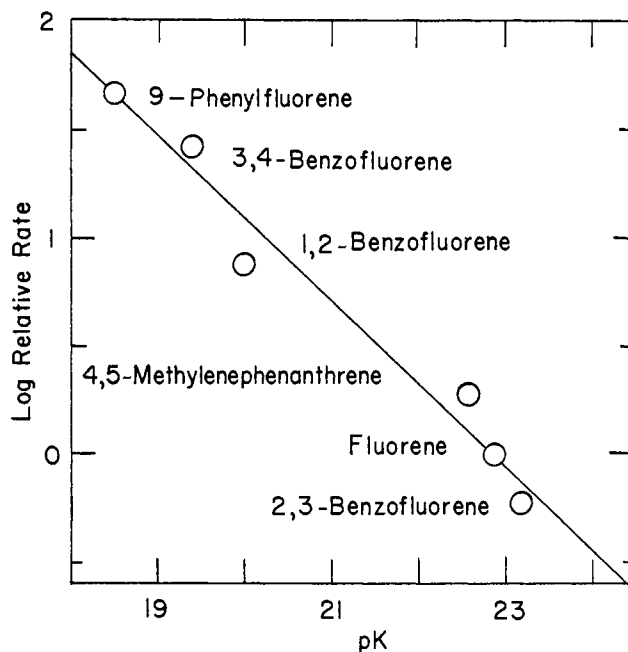


Figure 1. Brønsted plot of relative rates of hydrogen-tritium exchange of hydrocarbons in sodium methoxide-methanol at 44.9° compared with pK values in cyclohexylamine.

crease would be a little greater if allowance is made for the inductive effect of the alkyl bridge. Thus, of the 14 pK unit difference between triphenylmethane and 9-phenylfluorene, about one-third comes from the increased coplanarity of the rings in the latter carbanion and two-thirds from the distinctive anion-stabilizing ability of the five-membered ring.

The establishment of a quantitative acidity scale for hydrocarbons allows for the first time a rigorous test

of Brønsted's law for such systems. Fluorene exchanges its methylene hydrogens at a convenient rate for deuterium or tritium⁹ in methanol-sodium methoxide. At 44.9°, the second-order rate constant for tritium exchange, $10^4 k_2 = 3.68 + 2.3[\text{NaOCH}_3]$ (1. mole⁻¹ sec.⁻¹), shows a mild positive salt effect. The relative rates of several fluorene hydrocarbons in Table II give a fair Brønsted plot with $\alpha = 0.4$ (Figure 1). This correlation gains significance from the common use of exchange rates as measures of relative acidity.

(9) S. Andreades, *J. Am. Chem. Soc.*, **86**, 2003 (1964).

(10) (a) National Science Foundation Predoctoral Fellow, 1959-1962; (b) Fellow of the Indonesian AID Program.

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Long-Range Shielding Effect of a Cyclopropane Ring¹

Sir:

In recent years much interest has been shown in the long-range shielding effect of a three-membered ring, which has generally been ascribed to the ring current.² A recent theoretical study by Patel, Howden, and Roberts³ demonstrated that the comparison between experiment and theory cannot be used to establish the existence of ring current in cyclopropanes, but the trends are reasonably consistent with a ring-current effect. Burke and Lauterbur⁴ published further work dealing with the calculations based on a simple form of a ring-current model to account satisfactorily for the hydrogen and carbon magnetic shieldings and the magnetic susceptibility of cyclopropane itself. Since the chemistry of cyclopropane derivatives has received much attention in recent years, it seems desirable for their structure determination to estimate simply the shielding effects of a cyclopropane ring. Recently, Forsén and Norin⁵ estimated the anisotropy of a cyclopropane ring using the point dipole approximation. However, it seems to us that this approximation is too rough to predict the magnitude of the effect. On the other hand, the Johnson and Bovey method^{3,6} is thought to be tedious to carry out the calculation without availability of a computer or computation results in actual cases. Thus, we propose a simple method for rapid estimation of the magnitude of the long-range shielding effect of a cyclopropane

(1) N.m.r. Studies of Bridged Ring Systems Part VI. For Part V, see K. Tori, Y. Hamashima, and A. Takamizawa, *Chem. Pharm. Bull. (Tokyo)*, **12**, 924 (1964).

(2) K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961); J. D. Graham and M. T. Rogers, *ibid.*, **84**, 2249 (1962); B. P. Dailey, A. Gawer, and W. C. Neikam, *Discussions Faraday Soc.*, **34**, 18 (1962); J. Tadanier and W. Cole, *J. Org. Chem.*, **27**, 4610 (1962); R. R. Sauers and P. E. Sonnet, *Chem. Ind. (London)*, 786 (1963); R. S. Bojkess and S. Winstein, *J. Am. Chem. Soc.*, **85**, 343 (1963); P. R. Jefferies, R. S. Rosich, and D. E. White, *Tetrahedron Letters*, No. 27, 1853 (1963); K. Tori, K. Kitahonoki, Y. Takano, H. Tanida, and T. Tsuji, *ibid.*, No. 11, 559 (1964); M. S. Bergqvist and T. Norin, *Arkiv Kemi*, **22**, 137 (1964).

(3) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3218 (1963).

(4) J. J. Burke and P. C. Lauterbur, *ibid.*, **86**, 1870 (1964).

(5) S. Forsén and T. Norin, *Tetrahedron Letters*, No. 39, 2845 (1964).

(6) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

ring by employing McConnell's equation⁷ with an empirically deduced constant.

In order to evaluate the long-range shielding effect of a cyclopropane ring as exactly as possible we have to observe the n.m.r. spectra of a pair of compounds, one of which has a cyclopropane ring introduced into the other without any significant alterations in the geometry of the remaining part of the molecule.⁸ We prepared the six tricyclo[3.2.2.0^{2,4}]nonane derivatives¹⁰ I-VI to compare their n.m.r. spectra with those of the corresponding bicyclo[2.2.2]octane derivatives¹¹ which differ from the tricyclononanes only in the lack of the cyclopropane methylene. Table I shows the n.m.r. spectral data on these tricyclononanes and the values of additional signal shifts arising from the long-range shielding effects of an introduced cyclopropane ring. Thus the anisotropy of the shielding effect of a cyclopropane ring was disclosed clearly.

First we attempted to account for these anisotropic shielding effects by the ring-current model in the point dipole (at the center of a cyclopropane ring) approximation.^{7,12}

On the basis of the data in Table I and molecular geometries estimated with Dreiding models, the anisotropy value of a cyclopropane $\Delta\chi$ in the McConnell equation⁷ was evaluated to be about 35×10^{-30} cm.³/molecule, which is of the same order of magnitude as the values so far estimated by other workers.^{4,5} However, the calculated additional shift values by using this $\Delta\chi$ value do not agree well with those observed (Table I).

Increased p-character of a C-C bent bond of a cyclopropane ring¹³ might make a change in the magnitude of molecular anisotropy of an ordinary C-C bond (-5.5×10^{-30} cm.³/molecule).¹² Thus on the basis of the concept of bond anisotropy¹² instead of a ring current, we attempt to estimate additional shift values $\Delta\delta$ of an affected proton signal due to the shielding effect of a cyclopropane ring by eq. A, provided that R_i is fairly large⁷ (the contribution of C-H bonds was neglected), where R_i is the distance

$$\Delta\delta \text{ (p.p.m.)} = \frac{\Delta\chi}{3} \sum_{i=1}^3 \frac{3 \cos^2 \theta_i - 1}{R_i^3} \quad (\text{A})$$

in Å. between the midpoint of a C-C bond of a cyclopropane ring and an affected proton, θ_i is the acute angle which the line R_i makes with the C-C bond, and $\Delta\chi$ is an empirically deduced constant, to which in the present paper we tentatively gave a value of -20×10^{-30} cm.³/molecule, derived from the data in Table I.

(7) H. M. McConnell, *ibid.*, **27**, 226 (1957).

(8) Most of the earlier reported compounds in which the shielding effect of a cyclopropane ring was observed^{2,3,5} indicate appreciable changes in their molecular geometries owing to introduction of their cyclopropane ring, and, in addition, some of their geometries were not made clear because of lack of physical data or because of ignoring their molecular conformations (for example, tricyclo[3.2.1.0^{2,4}]octane derivatives,⁹ nortricyclenes, quadricyclenes, thujane derivatives, etc.).

(9) Also refer to W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28**, 2200 (1963); R. E. Pincock and J. I. Well, *ibid.*, **29**, 965 (1964).

(10) K. Alder and G. Jacobs, *Chem. Ber.*, **86**, 1528 (1953).

(11) K. Tori, Y. Takano, and K. Kitahonoki, *ibid.*, **97**, 2798 (1964).

(12) For example, see L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Chapter 7, Pergamon Press, New York, N. Y., 1959.

(13) G. S. Handler and J. H. Anderson, *Tetrahedron*, **2**, 345 (1958); N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768 (1959)