solution was heated to 150° for 5 min [(Me₂)₂Ni^{IV}] or 30 min (TM₂Ni^{IV}) and cooled and the absorption spectra were obtained to yield A_∞. The rate constants were obtained from linear plots of $-\log (A_t - A_\infty/A_0 - A_\infty)$ vs. t. Plots of log k vs. $1/T$ gave the activation parameters.

Acidity of Hydrocarbons. XXXIX. H_- Acidity Function for Methanolic Sodium Methoxide (H_M) Based on Ionization of a Hydrocarbon Acid[1]

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Abstract: pK values of 1,3-diphenylindene and fluoradene were determined to be 19.8 and 18.2, respectively, in methanol at 25°. An H_- scale for methanolic sodium methoxide (H_M) has been constructed from the ionization of 1,3-diphenylindene. This H_M scale gives an excellent linear correlation with the logarithm of the pseudo-first-order rate constants of base-catalyzed protodetritiation reaction of fluorene in NaOMe–MeOH.

The H_- acidity function[2] measures the ability of a basic medium to ionize an acid, HA, to form the anion A$^-$, and is defined as

$$H_- = \mathrm{p}K_{HA} - \log [HA]/[A^-] = -\log (a_H \cdot f_{A^-})/f_{HA} \tag{1}$$

For a methanol solution, pK_{HA} is the ionization constant of HA in methanol and the activity coefficient, f, refers to methanol as standard state. Several authors have used H_M for H_- in methanol, where the use of subscript, M, denotes the acidity function for methanol instead of water as standard state.

The existing H_M scales have been determined by using nitrogen and oxygen acids as indicators, whereas most kinetic investigations involve base-catalyzed breaking of C–H bonds. In fact, for acids of different structure the ratio f_{A^-}/f_{HA} cannot be assumed to be the same at a given solvent composition. Thus, $H_-(H_M)$ scales depend on the type of indicator used.[3,4] With substituted anilines and diphenylamines as indicators, H_M scales for methanolic sodium methoxide have been reported by Schaal and Lambert,[5] and More O'Ferrall and Ridd.[6] The two scales agree satisfactorily when the same value of pK_{MeOH} is used. Rochester[7] used o-tert-butylphenol, di-o-tert-butylphenol, and pentamethylphenol to set up three H_M scales which differ slightly from one another but differ substantially from the H_M acidity function derived from amine indicators.

Bowden and Stewart[8] constructed an H_- scale for the system DMSO–EtONa using only carbon acids as indicators. They started with malononitrile in water and established the pK values of 9-cyanofluorene, 9-methoxycarbonylfluorene, and tris- and bis(4-nitrophenyl)methane. The latter compound was compared with 9-phenylfluorene and with fluorene. However, it is by no means certain that the various substituted carbon acids used are really more similar to hydrocarbon acids than nitrogen acids. That is, an important contributor to variations in f_{A^-}/f_{HA} is hydrogen-bonding solvation toward A$^-$.[9] In the present work we report an H_M acidity function derived solely from hydrocarbons whose conjugate bases are delocalized carbanions for which hydrogen-bonding solvation is minimal.

Experimental Section

The preparations of 1,3-diphenylindene, DPI, and fluoradene, FD, have been described.[10] The sodium methoxide solutions were prepared by adding freshly cut and cleaned sodium to cooled absolute methanol under argon or nitrogen atmosphere. The resulting sodium methoxide solutions were degassed on the vacuum line and pressured with argon. The sodium methoxide concentrations were determined by titration with standard acid.

Since the carbanions studied here are sensitive to air, all materials were handled under an argon atmosphere. The apparatus for equilibrium measurements has been described.[11] For runs in which the sodium methoxide concentration was less than 0.5 M. a modified apparatus was used in which a cylindrical Pyrex absorption cell of path length 4.54 cm replaced the 1.00-cm cell. The solid hydrocarbon was added to either apparatus which was then attached to the vacuum line and evacuated. The entire system was pressured with argon. A known amount of degassed absolute methanol was added to the apparatus and the mixture was shaken until the hydrocarbon dissolved. A known amount of sodium methoxide solution was introduced by a syringe. After mixing

(1) This research was supported in part by Grant No. 12855 of the National Institutes of Health, U. S. Public Health Service.

(2) (a) L. P. Hammett and A. J. Deyrup, *J. Amer. Chem. Soc.*, **54**, 2721 (1932); (b) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957); (c) K. Bowden, *ibid.*, **66**, 119 (1966).

(3) E. C. Steiner and J. D. Starkey, *J. Amer. Chem. Soc.*, **89**, 2751 (1967).

(4) R. H. Boyd, *ibid.*, **85**, 1555 (1963).

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(6) R. A. More O'Ferrall and J. H. Ridd, *J. Chem. Soc.*, 5030 (1963).

(7) (a) C. H. Rochester, *Quart. Rev., Chem. Soc.*, 511 (1966); (b) C. H. Rochester, "Acidity Functions," Academic Press, London and New York, 1970, Chapter 7.

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

(9) C. D. Ritchie in "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, p 219.

(10) A. Streitwieser, Jr., C. J. Chang, and W. Hollyhead, *J. Amer. Chem. Soc.*, in press.

(11) A. Streitwieser, Jr., J. H. Hammons, E. Ciuffarin and J. I. Brauman, *J. Amer. Chem. Soc.*, **89**, 59 (1967); G. Häfelinger and A. Streitwieser, Jr., *Chem. Ber.*, **101**, 657 (1968).

the reactants, the visible spectrum of carbanion was taken with a Perkin-Elmer 202 spectrophotometer when the solution had reached temperature equilibrium in the cell compartment (34°). Additional base or methanol was added as appropriate, and spectra at different sodium methoxide concentrations were obtained.

Results and Discussion

pK Values in Methanol. Both 1,3-diphenylindene, DPI, and fluoradene, FD, ionize in NaOMe–MeOH to produce color according to eq 2. Table I lists the spec-
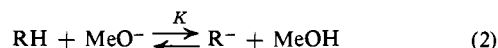
$$RH + MeO^- \underset{K}{\overset{K}{\rightleftharpoons}} R^- + MeOH \qquad (2)$$

Table I. Spectral Data for Hydrocarbon Anions

Hydrocarbon	λ_{max} in NaOMe–MeOH[a]	λ_{max} (ϵ_{max}) in CsCHA–CHA[a,b]
1,3-Diphenylindene	370, 420	384 (21,500), 428 (21,850)
Fluoradene	362, 376, 536	364, 380, 518 (3400), 556 (4200)

[a] mμ.   [b] See ref 10.

tral results of DPI and FD in NaOMe–MeOH and in cesium cyclohexylamide–cyclohexylamine (CsCHA–CHA).[10] Since reaction 2 does not completely go to the right, the extinction coefficients of sodium salts in methanol cannot be determined. Therefore, the extinction coefficients of cesium salts in CHA were used to calculate the carbanion concentration. Extinction coefficients of related carbanion salts generally vary by less than 20% with different solvents and cation gegenions.[12] However, even an error of 20% in ϵ would produce an error of less than 0.1 in the hydrocarbon pK value.

The procedure of More O'Ferrall and Ridd[6] was used to determine the pK values in methanol. The concentration equilibrium constant K_c depends on the sodium methoxide concentration; that is, in the H_- acidity function concept the equilibrium constant of a neutral acid RH

$$K_b = a_{RH} a_{MeO^-} / a_{R^-} a_{MeOH} \qquad (3)$$

is related to the indicator ratio R (= [R$^-$]/[RH]) and the NaOMe concentration by eq 4. If the activities of

$$pK_b = \log R - \log [MeO^-] +$$
$$\log (f_{R^-} a_{MeOH} / f_{RH} f_{MeO^-}) \qquad (4)$$

methanol and f_{RH} are taken as unity, the last term of eq 4 becomes equal to zero in infinitely dilute solution. A plot of ($\log R - \log [MeO^-]$) against [OMe$^-$] therefore leads to the value of pK_b when extrapolated to [MeO$^-$] = 0. Table II shows the indicator ratio for DPI at different base concentrations. Figure 1 gives the plot of ($\log R - \log [OMe^-]$) against [OMe$^-$]. The plot is linear over a concentration range from [NaOMe] = 0.1 M, where the base is largely dissociated, to [NaOMe] = 2.5 M, where ion pairing must be substantial. A linear function to such concentrated solutions is clearly not required and we have no simple explanation, but the observed linearity does facilitate a precise extrapolation to zero base concentration which gives the value −2.83 ± 0.01 for the pK_b of DPI at 34°. For several solutions, the spectra were also taken at 25°; the

(12) For example, see the summary in G. Häfelinger and A. Streitwieser, Jr., *ibid.*, **101**, 2758 (1968).
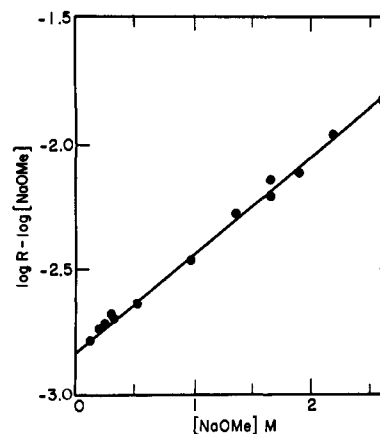

Figure 1. Extrapolation for pK_b of 1,3-diphenylindene in methanolic sodium methoxide. Equation of line is: ordinate = (0.395 ± 0.009)[NaOMe] − 2.829 ± 0.012; r = 0.997.

corresponding pK difference is 0.08 ± 0.02. Thus, the pK_b of DPI at 25° is −2.91 ± 0.03. The pK_a is then calculated from the ionic product of methanol at 25°, $10^{-16.92}$;[13] pK_a = pK_{MeOH} − pK_b = 16.92 + 2.91 = 19.83. The pK_a so obtained is referred to the infinitely dilute methanol solution as the standard state.

Table II. 1,3-Diphenylindene in NaOMe–MeOH

A^{420} nm	[R$^-$],[a] $10^5 M$	[RH], $10^3 M$	[OMe$^-$], M	Log R − log [MeO$^-$]
0.057[b]	0.058	2.90	0.123	−2.793
0.082[b]	0.082	2.32	0.196	−2.741
0.087[b]	0.088	1.93	0.245	−2.732
0.095[b]	0.096	1.65	0.280	−2.683
0.080[b]	0.081	1.29	0.326	−2.717
0.077[c]	0.352	2.97	0.526	−2.644
0.200[c]	0.915	2.71	0.965	−2.456
0.385[c]	1.76	2.49	1.34	−2.278
0.602[c]	2.76	2.30	1.65	−2.138
0.263[c]	1.20	1.15	1.65	−2.200
0.330[c]	1.51	1.00	1.93	−2.109
1.075[c]	4.92	1.99	2.17	−1.944
1.481[c]	6.78	1.74	2.57	−1.820

[a] The extinction coefficient was taken as 21,850 from CsCHA solutions (Table I).   [b] 4.54-cm cell.   [c] 1.00-cm cell.

The same method was followed for fluoradene with less success, the main difficulty being low solubility of FD in NaOMe–MeOH solution. When the base concentration was set higher than 1 M, the solution soon turned cloudy and a precipitate was formed during spectral scanning; consequently, the results at higher base concentrations are not reliable. When the indicator ratios of the two experimental points at lowest base concentration were used, a pK_b of −1.28 was obtained from the extrapolation of the two-point line, which gives 18.20 for the pK_a of FD in MeOH at 34°. Using the H_M values obtained from DPI in the following section and the indicator ratios of these two points, pK_a values of 18.14 and 18.08 (at 34°) were obtained which are in good agreement with the direct value of 18.20. We assume the same temperature effect as for DPI and take 18.20 as the best value for the pK_a of FD at 25°.

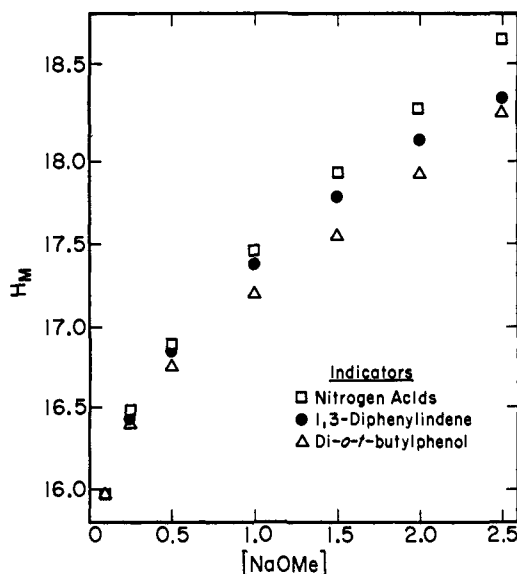(13) J. Koskikallio, *Suom. Kemistilehti B*, **30**, 111 (1957).

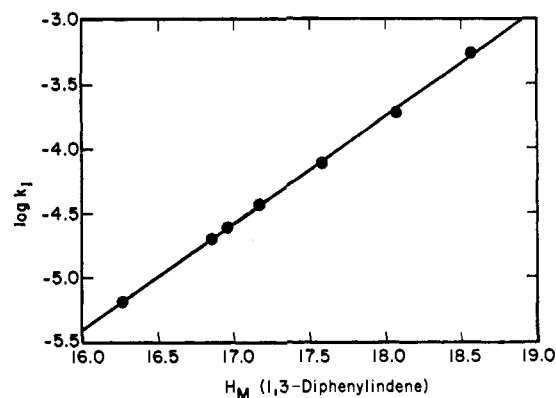Figure 2. H_M values for methanolic sodium methoxide solutions as determined by different indicators.

Figure 3. Pseudo-first-order rate constants for tritium exchange of fluorene-9-t with methanolic sodium methoxide as a function of H_M values for 1,3-diphenylindene as indicator.

Ritchie and Uschold reported[14] a pK value of 10.5 for fluoradene in DMSO. This value for a DMSO standard state is 7.7 units lower than our pK of 18.2 for MeOH as standard state. The pK values in different standard states are related through the "degenerate activity coefficients," defined by Grunwald and Berkowitz.[15] The higher dielectric constant and greater basicity[14] of solvent should increase the acidity of an acid in DMSO. Counterbalancing the relative electrostatic effects and the basicities of the two solvents, any hydrogen bonding toward the conjugate anion would increase the acidity in methanol. However, such hydrogen bonding is expected to be insignificant with a highly delocalized carbanion. Whether the electrostatic effect and the solvent basicity alone can accommodate a 7.7-pK unit difference between the two solvent systems has not yet been established. Ritchie and Uschold[14,16] suggest that dispersion interactions of the delocalized anions with the highly polarizable DMSO solvent are more important than dispersion in methanol, and that this effect contributes to part of the pK difference between the two solvents. However, the magnitude of this effect has not been determined and its contribution could well be insignificant. The ΔpK (MeOH–DMSO) of 7.7 discussed above for FD may be compared with the values of 5.8 and 5.5 found by Ritchie[16c] for 9-cyanofluorene and 9-carbomethoxyfluorene, respectively; that is, these substituted fluorenes are relatively more acidic in methanol compared to DMSO than is the hydrocarbon, FD. This difference suggests some additional stabilization of the heterosubstituted carbanions by hydrogen-bonding solvation in methanol.

H_M **Acidity Function.** H_M values were calculated from eq 5 in which b is the slope in Figure 1. Table III

$$H_M = pK_a + \log R = pK_{MeOH} +$$
$$\log [NaOMe] + b[NaOMe] \quad (5)$$

(14) C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, 90, 2821 (1968).

(15) E. Grunwald and B. Berkowitz, *ibid.*, 73, 4939 (1951).

(16) (a) C. D. Ritchie and R. E. Uschold, *ibid.*, 89, 1721 (1967); (b) C. D. Ritchie and R. E. Uschold, *ibid.*, 89, 2752 (1967); (c) C. D. Ritchie, *ibid.*, 91, 6749 (1969).

Table III. Acidity Function Scales for Methanolic Sodium Methoxide

[NaOMe], M	$H_M{}^a$	$H_M{}^b$	$H_M{}^c$
0.10	15.97	15.97	
0.25	16.42	16.40	16.48
0.50	16.82	16.75	16.88
1.00	17.32	17.19	17.45
1.50	17.69	17.55	17.93
2.00	18.01	17.92	18.32
2.50	18.31	18.29	18.74
3.00			19.20

[a] The indicator is 1,3-diphenylindene. [b] The indicator is di-o-tert-butylphenol; ref 7a. The scale is corrected to accord with pK_{MeOH} = 16.92 rather than 16.7. [c] The indicator is nitrogen acids; ref 6. This scale is also corrected to pK_{MeOH} = 16.92.

shows the H_M values generated from the results with DPI. The more limited results with FD can be taken as establishing some generality for these H_M values. The H_M functions of other workers using phenol and nitrogen acids as indicators are included in Table III for comparison. Figure 2 was plotted from Table III and shows that the H_M function is not unique but varies with the particular indicators used to measure it.

One can rewrite eq 2 as

$$RH + MeO^-(MeOH)_n \rightleftharpoons R^- + (n + 1)MeOH \quad (6)$$

in which the factor n can be taken either as the solvation number of the OMe⁻ ion or as the difference in solvation numbers between RH + OMe⁻ and R⁻. In either case one can write

$$H_M = -\log a_{H^+} - \log (f_{R^-}/f_{RH}) = pK_{RH} +$$
$$\log ([R^-]/[RH]) = pK_{MeOH} + \log [OMe^-] -$$
$$(n + 1) \log a_{MeOH} + \log (f_{RH} f_{OMe^-}/f_{R^-}) \quad (7)$$

Inspection of eq 7 leads to the conclusion that deviations in H_M may be due to the effect of variation of structure on either log (f_{RH}/f_{R^-}) or n. Since one expects some differences in solvation among hydrocarbons, phenols, and aromatic amines, and particularly among their anions in methanol, it is not surprising that H_M values vary with the measuring indicators. The results clearly show that no single H_M acidity function applicable to acids of different structure can be constructed.

Correlation of H_M with Reaction Rates. A few reports on the correlations between H_- and rates of

base-catalyzed reactions have appeared in the literature.[6,17-19] A particularly significant reaction in the present context is the protodetritiation of fluorene in MeOH–NaOMe recently reported from this laboratory.[20] The pseudo-first-order rate constants for this

(17) R. Stewart, J. P. O'Donnell, D. J. Cram, and B. Rickborn, *Tetrahedron*, **18**, 917 (1962).

(18) W. D. Kollmeyer and D. J. Cram, *J. Amer. Chem. Soc.*, **90**, 1784 (1968).

(19) M. Anbar, M. Bobtelsky, D. Samuel, B. Silver, and G. Yagil, *ibid.*, **85**, 2380 (1963).

(20) A. Streitwieser, Jr., W. B. Hollyhead, A. H. Pudjaatmaka, P. H. Owens, T. L. Kruger, P. A. Rubenstein, R. A. MacQuarrie, M. L. Brokaw, W. K. C. Chu, and H. M. Niemeyer, *ibid.*, **93**, 5088 (1971).

exchange reaction give curved correlations with H_M functions derived from the nitrogen and oxygen acids.

The correlation with the present H_M acidity function derived from the related hydrocarbon, DPI, is presented in Figure 3. Although this correlation is accurately linear over this range with a least-squares slope of 0.847 $\pm$ 0.006, over the whole range of $NaOCH_3$ concentrations the correlation mnst be nonlinear; that is, this line applies only at relatively high base concentrations ($H_M > 16$). At low $NaOCH_3$ concentrations, where the second-order rate constant is essentially constant, a line of unit slope is expected.

Mechanism of Transmission of Nonconjugative Substituent Effects. IV. Analysis of the Dissociation Constants of 6-Substituted Spiro[3.3]heptane-2-carboxylic Acids[1,2]

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Abstract: The pK_a's of eight 6-substituted spiro[3.3]heptane-2-carboxylic acids in 50% (by weight) aqueous ethanol at 25° are presented. Excellent correlation is obtained between the experimental data and σ_I parameters, whereas only a fair correlation is obtained using the Dewar-Grisdale F parameters. The data are also analyzed by means of the Tanford modification of the Kirkwood-Westheimer cavity model. Excellent agreement between calculated and experimental results is obtained with the spherical cavity model as well as with Stock's modification of this electrostatic model. An analysis is presented which demonstrates that hydrogen and methyl substituents do not exhibit anomalous behavior when compared to more polar substituents by means of the cavity models. Analysis of the limiting models for the propagation of nonconjugative substituent effects (σ-inductive and field) suggests that the field model is more reliable in explaining the data.

The electrostatic approaches to quantitatively describing the effects of dipolar and charged substituents on the dissociation constants of organic acids are well known.[3-5] The most theoretically satisfying is the model of Kirkwood and Westheimer[6] which views the charges or dipoles as being embedded in a structureless spherical or ellipsoidal cavity of low dielectric constant immersed in a structureless solvent of high dielectric constant. Roberts and Moreland[7] have examined this model with a series of 4-substituted bicyclo-[2.2.2]octane-1-carboxylic acids. Discrepancies were observed between theory and experiment and were of such a serious nature that Tanford[8] reexamined and

modified the electrostatic model. He considered that the important parameter in evaluating interaction energies is the depth at which the dipole or charge is placed within the cavity. Siegel and Kormarmy[9] determined the pK_a value of a series of trans-4-substituted cyclohexane-1-carboxylic acids in several solvent systems and found that both models were qualitatively acceptable but still inadequate quantitatively. Stock and Holtz[10,11] have reexamined and extended the work of Roberts and Moreland. Nevertheless, even with the improved data, the discrepancy between theory and experiment still remained significant.

Dewar and Grisdale[12] have proposed a model for field effect based upon the ionization constants of meta-substituted benzoic acids. In this treatment, they criticize the point dipole model for relatively small molecules in which the length of the dipole is comparable to the distance separating it from the reaction center and contend that the important distance parameter is an r^{-1} term rather than r^{-2} as in the Kirkwood-Westheimer treatment. Stock,[10,11] however, has attempted to apply Dewar's field approach to the 4-sub-

(1) Part III: C. L. Liotta, W. F. Fisher, E. L. Slightom, and C. L. Harris, *J. Amer. Chem. Soc.*, **94**, 2129 (1972); part II: C. L. Liotta, W. F. Fisher, and C. L. Harris, *J. Chem. Soc. D*, 1312 (1971); part I: C. L. Liotta, W. F. Fisher, and G. H. Greene, Jr., *ibid.*, 1251 (1969).

(2) Abstracted in part from the Ph.D. thesis of W. F. F., Georgia Institute of Technology, 1970, and from the M.S. Thesis of B. L. J., Georgia Institute of Technology, 1971.

(3) N. Bjerrum, *Z. Phys. Chem.*, **106**, 219 (1923).

(4) A. Eucken, *Angew. Chem.*, **45**, 203 (1932).

(5) H. M. Smallwood, *J. Amer. Chem. Soc.*, **54**, 3048 (1932).

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(7) J. D. Roberts and W. T. Moreland, *J. Amer. Chem. Soc.*, **75**, 2167 (1953).

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(11) F. W. Baker, R. C. Parish, and L. M. Stock, *ibid.*, **89**, 5677 (1967).

(12) M. J. S. Dewar and J. Grisdale, *ibid.*, **84**, 3539, 3548 (1962).