106. *Acidity Functions in Strongly Basic Media. Part I. The Ionisation of Phenols in Concentrated Methanolic Sodium Methoxide Solutions.*

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The ionisation equilibria of six phenols in methanolic sodium methoxide solution (10^{-3}M < [NaOMe] < 4·2M) have been studied by ultraviolet spectrophotometry. The results are consistent with the definition of an acidity function which differs from the H_- function measured, substituted anilines and diphenylamines being used as indicators.

Measurement of the H_- acidity function [1] for methanolic sodium methoxide solutions has been made, substituted anilines and diphenylamines being used as indicators on the assumption that they ionise by a proton transfer to the base substrate.[2,3]

Recent measurements of the ionisation of weak bases in concentrated acid solutions have shown that the protonation of certain bases, notably phenols [4] and amides,[5,6] is not consistent with the accepted Hammett acidity functions (H_0) [1,7] for the acid media. Differences between the protonation equilibria of amides or phenols and true Hammett bases can be satisfactorily explained by assuming different degrees of solvation of the conjugate acids of the indicators.[4,5] However, although any difference between the protonation equilibria in acid solution of different classes of base may afford information about the solvation of carbonium ions, it will also place a limitation upon the use of H_0 as a criterion of mechanism.[6] A similar argument would apply if the H_- function were not independent of the class of acid used to measure it.[8] The present work is an attempt to establish an H_- function for methanolic sodium methoxide solutions using acid indicators dissimilar in structure to those already investigated.

The ionisation of several phenols in ethanol–water containing sodium hydroxide has been studied by Coggeshall and Glessner.[9] The range of sodium hydroxide concentration in which a phenol was converted into its anion was affected markedly by the presence of t-butyl groups *ortho* to the phenol group. A series of spectra of a given phenol in different sodium hydroxide concentrations failed to show isosbestic points but this may be due to the use of a mixed ethanol–water solvent.

[1] Paul and Long, *Chem. Rev.*, 1957, **57**, 1.
[2] Schaal and Lambert, *J. Chim. phys.*, 1962, 1164.
[3] More O'Ferrall and Ridd, *J.*, 1963, 5030.
[4] Kresge, Barry, Charles, and Chiang, *J. Amer. Chem. Soc.*, 1962, **84**, 4343.
[5] Edward and Wang, *Canad. J. Chem.*, 1962, **40**, 966.
[6] Katritzky, Waring, and Yates, *Tetrahedron*, 1963, **19**, 465.
[7] Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721.
[8] Stewart and O'Donnell, *J. Amer. Chem. Soc.*, 1962, **84**, 493.
[9] Coggeshall and Glessner, *J. Amer. Chem. Soc.*, 1949, **71**, 3150.

The ionisation reactions of six t-butyl substituted phenols in methanolic sodium methoxide solutions have now been studied. The results are consistent with the definition of an H_- acidity function.

Experimental

The phenols were purified by repeated recrystallisation from aqueous ethanol or benzene.[10,11] *o*-t-Butylphenol was purified by distillation under reduced pressure.[11] Owing to the instability of the pure phenols a stock solution of each in methanol (dried by standard method [12]) was prepared immediately after purification. The stock solutions, when stored in the dark, were stable for the period over which ionisation measurements were made.

Samples of liquid sodium under argon were obtained from the liquid metals laboratory of this department. The total alkalinity content determined by titration of the residue after sodium distillation and expressed as oxygen content was 6—8 p.p.m. On solution in dried methanol clear stable sodium methoxide solutions resulted. These were estimated by titration with standard aqueous hydrochloric acid.

Reaction mixtures were prepared by weighing stock sodium methoxide solution into graduated flasks, adding a known volume of phenol solution, and making to the mark with methanol. Spectra were determined on a Unicam S.P. 800 spectrophotometer, and optical density measurements at two wavelengths were made on a Unicam S.P. 500 spectrophotometer with a thermostated cell compartment (25°). The wavelengths selected for study were close to the two absorption maxima of the conjugate bases of the phenols. All spectra investigations were made using 1-cm. stoppered silica cells, the blank cell containing sodium methoxide solution of the same concentration as that in the reaction solution under test.

Nuclear magnetic resonance (n.m.r) spectra of 2,6-di-t-butylphenol and 2,6-di-t-butyl-4-methylphenol in chloroform, methanol, and sodium methoxide solutions in methanol were recorded on an AEI RS2 instrument operating at 60 Mc./sec. Concentrations of phenol were ~0·5M. The methoxide concentrations were selected so as to ensure at least 25% conversion into the phenol anion and so that the alcohol proton signal did not occur at the same field as the phenol proton or ring proton signals of the phenols.

Results and Discussion

A comparison of the n.m.r. spectra of 2,6-di-t-butylphenol or 4-methyl-2,6-di-t-butyl phenol in chloroform and in methanolic sodium methoxide show that the positions of the ring protons, methyl protons, and t-butyl protons are unaffected by the solvent change. However, the phenol proton peak present in chloroform is absent in the base solutions. This suggests that in sodium methoxide solution the phenol proton is rapidly exchanging with the alcohol proton of the solvent and the phenol signal is coalescing with the alcohol proton signal at lower field. This would support the ionisation of the phenols in the base media as being the expected proton transfer

$$ROH + OMe^- \rightleftharpoons RO^- + MeOH$$

A typical series of ultraviolet spectra is shown in Fig. 1. The spectra for the other phenols were very similar and where isosbestic points were present they were very well defined. A summary of the wavelengths and extinction coefficients of the absorption maxima for the neutral phenols and their conjugate bases is given in the Table.

Apart from 4-methyl-2,6-di-t-butylphenol, discussed below, pK_a values (Table) for the phenols were deduced by the method of More O'Ferrall and Ridd.[3] *p*-t-Butylphenol showed ideal behaviour in the sodium methoxide concentration range 10^{-3}M < [NaOMe] < 0·5M. Thus $\log R - \log$ [NaOMe] (where $R = [RO^-]/[ROH]$) was a constant, giving $pK_b = 2{\cdot}269$, standard deviation $\sigma = \pm 0{\cdot}004$, and hence, taking the ionic product of methanol as $pK_s = 16{\cdot}70$,[13] giving 14·43 for pK_a. For the other phenols, $\log R -$ log [NaOMe] was not constant and therefore extrapolation to zero concentration of sodium methoxide was necessary to evaluate pK_b. Values of R were calculated from each of the

[10] Stillson, Sawyer, and Hunt, *J. Amer. Chem. Soc.*, 1945, **67**, 303.
[11] Pardee and Weinrich, *Ind. Eng. Chem.*, 1944, **36**, 595.
[12] Reverdin, *Org. Synth.*, 1927, **7**, 29.
[13] Bell, " The Proton in Chemistry," Methuen, London, 1959, p. 46.

two wavelengths studied and the mean taken. The numerical order of pK_a (2,4,6 > 2,6 > 2,4 > *ortho* > *para*) is consistent with the expected steric and electronic effects of *o*- and *p*-t-butyl groups upon the ionisation of a phenolic proton.

4-Methyl-2,6-di-t-butylphenol (~10^{-4}M) was unstable in sodium methoxide solution and extrapolation to zero time of a series of optical density measurements was necessary. The instability was most probably caused by traces of dissolved oxygen in the solvent methanol.[14-16] Thus a sealed sample containing phenol (0·4M) and sodium methoxide (2·1M) contained 94% of unchanged phenol after 14 days. Initial reaction spectra were similar to those in Fig. 1 and up to [NaOMe] = 3M showed three well-defined isosbestic

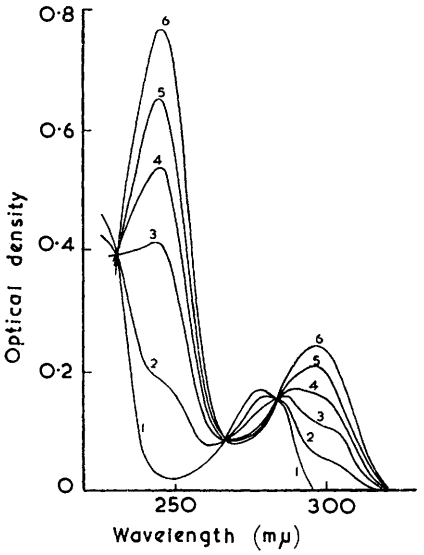

FIG. 1. Absorption spectra of 2,4-di-t-butylphenol in sodium methoxide solutions.

[ROH] = 7·43 × 10^{-5}M.

[NaOMe]: (1) 0; (2) 0·18M; (3) 0·53M; (4) 0·88M; (5) 1·41M; (6) 2·54M.

Spectral data and pK_a for neutral phenols, and absorption maxima of phenol anions.

	Neutral phenols			Phenol anions			
	pK_a	λ_{max} (mμ).	$10^{-3}\,\varepsilon_{max.}$	λ_1 (mμ)	$10^{-4}\,\varepsilon_1$	λ_2 (mμ)	$10^{-4}\,\varepsilon_2$
p-t-Butylphenol	14·43	277	1·86	239	1·21	294	0·25
o-t-Butylphenol	16·25	274	2·24	244	0·88	291	0·36
2,4-Di-t-butylphenol	16·53	278	2·29	245	1·08	296	0·34
2,6-Di-t-butylphenol	17·08	272	1·60	251	0·90	298	0·52
2,4,6-Tri-t-butylphenol	17·40	274	1·58	252	1·02	302	0·44
4-Methyl-2,6-di-t-butylphenol	~17·50	279	1·84	254	~0·82	307	~0·49

points. However, in [NaOMe] > 3M the isosbestic points were absent suggesting possibly general solvent effects [17] and preventing accurate determination of the spectral characteristics of the conjugate base. Rough estimates of extinction coefficients (±20%) and pK_a (±0·3) are given in the Table.

The H_- acidity functions suggested by the ionisation equilibria of each phenol were calculated from the equation

$$H_- = pK_a + \log_{10}([RO^-]/[ROH]) \quad (1)$$

The dependence of H_- on stoicheiometric sodium methoxide concentration for four of the phenols is shown in Fig. 2. The results for 4-methyl-2,6-di-t-butylphenol, athough agreeing very well, have been ignored in view of their uncertainty. The H_- function given by the ionisation equilibria of substituted anilines and diphenylamines [3] has been included

[14] Yohe *et al.*, *J. Amer. Chem. Soc.*, 1953, **75**, 2688; *J. Org. Chem.*, 1956, **21**, 1289; 1959, **24**, 1251.
[15] Gersmann and Bickel, *J.*, 1959, 2711.
[16] Kharasch and Joshi, *J. Org. Chem.*, 1957, **22**, 1439.
[17] Parker and Brody, *J.*, 1963, 4061.

in Fig. 2 for comparison with the present scale. The two functions differ by up to 0·5 unit in 3M-sodium methoxide and plots of log R for the phenols against the acidity function established from amine equilibria were linear and had the following slopes: *o*-t-bu, 0·78; 2,4-di-t-bu, 0·76; 2,6-di-t-bu, 0·86; 2,4,6-tri-t-bu, 0·86. As has been stressed [18] the accuracy of such plots may be 0·1—0·2 slope unit in error.

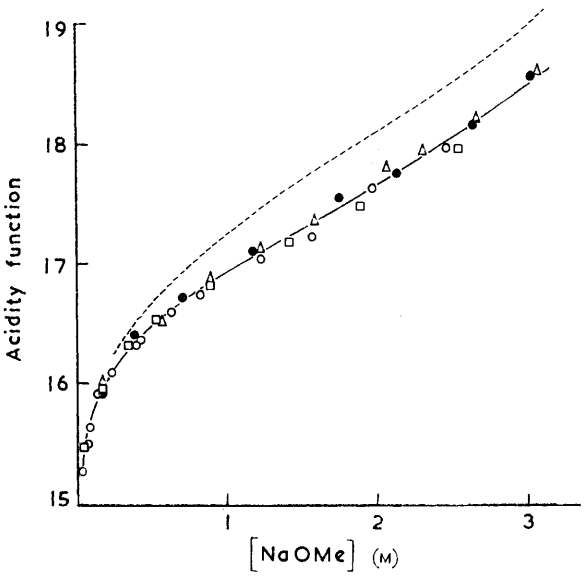

FIG. 2. H_- acidity function as defined by (– – – –) substituted amines,[3] (————) phenols (○ *ortho*; □ 2,4; △ 2,6; ● 2,4,6).

However, in this instance the agreement between four indicators of the same structural class is striking and the difference between acidity functions defined by two sets of indicators of dissimilar structural class must be taken as definite. We exclude the possibility that the small difference in temperature between the two sets of measurements could account for the discrepancy.

In acid media the deviation between acidity functions derived from ionisation equilibria of phenols or amides and true Hammett bases has been explained by assuming different degrees of solvation for the conjugate acids of the neutral indicators.[4,5] By analogy the ionisation of a neutral indicator BH in sodium methoxide solution can be written

$$BH + OMe^- \rightleftharpoons B^- + (n + 1)MeOH$$

where n represents the difference in solvation number between ($BH + OMe^-$) and B^-.[19] From the definition of H_- in equation (1) it follows that

$$H_- = pK_{MeOH} + \log [OMe^-] - (n + 1) \log a_{MeOH} + \log (f_{OMe^-}/f_{BH}/f_{B^-}) \qquad (2)$$

Hence deviations between acidity functions defined by structurally dissimilar indicators could result either from differences in the solvation factor n or from differences in the activity coefficient ratios f_{BH}/f_{B^-}.

Equation (2) cannot be adequately tested owing to lack of data on activities of methanol in sodium methoxide solutions. Calculations similar to those of Yagil and Anbar [20] for prediction of the H_- function in aqueous sodium hydroxide solutions are not possible as they would require assumption of a solvation number for the methoxide ion.

The author thanks Mr. T. Buckley for measurement of the n.m.r. spectra, Dr. R. J. Pulham for gifts of pure liquid sodium, and Dr. H. Booth for helpful discussion.

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[18] Arnett and Anderson, *J. Amer. Chem. Soc.*, 1963, **85**, 1542.
[19] Edward and Wang, *Canad. J. Chem.*, 1962, **40**, 399.
[20] Yagil and Anbar, *J. Amer. Chem. Soc.*, 1963, **85**, 2376.