855. *A Comparison of the Acid Ionisation Constants of* p-*t-Butylphenol,* o-*t-Butylphenol, and 2,4-Di-t-butylphenol in Water and Methanol*

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In methanol, t-butylphenols are sufficiently weak acids to be used as indicators for H_- acidity function measurements.[1] However it appears unlikely that their use can be extended to aqueous solutions as even 2,6-di-t-butylphenols would be completely converted into their phenoxide anions in less concentrated base solutions than are normally of interest from the acidity function point of view. The acid ionisation constants at 25° of three t-butylphenols in aqueous solution are now reported.

Ultraviolet spectra of the undissociated phenols and their phenoxide anions were recorded. Series of spectra for each phenol in standard carbonate or phosphate buffers[2] were measured, and ionisation ratios $R = [\mathrm{PhO^-}]/[\mathrm{PhOH}]$ were evaluated from extinction coefficients at the two wavelengths corresponding to the absorption maxima of the anions. The spectra showed good isosbestic points as before.[1] Values of pK_a for the phenols were deduced from the equation[3]

$$\mathrm{p}K_a = \mathrm{pH} - \log_{10}R + \{0{\cdot}5115\sqrt{I}/1 + \sqrt{I})\} - 0{\cdot}2I$$

Ionic strengths I were taken from Bates and Bower.[2] The pH values ($= -\log_{10}m_{\mathrm{H}^+}\gamma_{\mathrm{H}^+}$) were not corrected for the effect of the ionisation of phenols. This correction would only be of the order of 0·005, whereas the accuracy in pH suggested by Bates and Bower is ±0·02 unit. The pK_a values obtained are compared in the table with those in methanol solvent.

	pK_a (25°) (MeOH)	pK_a (25°) (HOH)	Literature values pK_a (HOH)	pK_r (MeOH)	pK_r (HOH)
Phenol	14·10[a]	9·97[c]		0	0
p-t-Butylphenol	14·43[b]	$10{\cdot}23_2$	10·23 (25°)[d] 10·25 (20°)[e]	0·33	0·26
o-t-Butylphenol	16·25[b]	$11{\cdot}33_6$		2·15	1·37
2,4-Di-t-butylphenol	16·53[b]	$11{\cdot}56_9$	$11{\cdot}71_5$ (20°)[e]	2·43	1·60
2,6-Di-t-butylphenol	17·08[b]	*	(11·70) † (25°)[d]	2·98	(1·73)
2,4,6-Tri-t-butylphenol	17·40[b]	*	(12·19) † (25°)[d]	3·30	(2·22)

[a] Ref. 4. [b] Ref. 1. [c] Ref. 5. [d] Ref. 6. [e] Ref. 7.

* These phenols were too insoluble in water for spectral measurements.[6,7] † Values predicted from Hammett σ plot for 4-substituted 2,6-di-t-butylphenols.[6]

Comparison of ionisation constants in different solvents are best made *via* the equilibrium constants K_r for the reaction

$$\mathrm{Ph^1OH + PhO^- \rightleftharpoons Ph^1O^- + PhOH}$$

where Ph^{1}OH represents the particular phenol under investigation and PhOH represents unsubstituted phenol.[8] Values of pK_r [$=\mathrm{p}K_a(\mathrm{Ph^1OH}) - \mathrm{p}K_a(\mathrm{PhOH})$] pertinent to the present study are given in the Table. Values of K_r in a given solvent can then be related from electrostatic considerations to the dielectric constant of the solvent.[8,9] However, the changes in pK_r for *o*-t-butylphenols in going from methanol to water are unexpectedly

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large if only dielectric effects are involved. Also if the predictions by Cohen and Jones[6] of pK_a for 2,6-di-t-butylphenol (11·70) and 2,4,6-tri-t-butylphenol (12·19) are taken as reasonable, the change in pK_r for 2,6-di-t-butyl substituted phenols would be even greater.

The results would be more compatible with the possibility that steric inhibition to solvation of the phenoxide anions is a contributing factor to the large increase in pK_a on introducing an *o*-t-butyl group into a phenol.[10] One might estimate that this effect would be smaller the smaller the solvent molecules and this is consistent with the observed deviation between the pK_r values of *o*-t-butyl substituted phenols in methanol and water. Steric inhibition to solvation of the phenoxide anions of *o*-methylphenols in water has also been suggested from calorimetric studies of the heats of neutralisation of cresols and xylenols.[11] It must be noted that the increase in pK_a on introducing *o*-t-butyl groups into a phenol can not be explained in terms of a non-bonding repulsion of the phenolic protons by the bulky *o*-t-butyl groups as this would lead to an increase in acidity, or a decrease in pK_a.[10]

Measurements of indicator ionisation ratios for the equlibrium, in methanolic sodium methoxide,

$$\mathrm{PhOH} + \mathrm{OMe}^- \rightleftharpoons \mathrm{PhO}^- + (n + 1)\mathrm{MeOH}$$

(where n is the difference in solvation between PhOH + OMe$^-$ and PhO$^-$) provides an H_- acidity function given by[1]

$$H_- = \mathrm{p}K_{\mathrm{MeOH}} + \log_{10}[\mathrm{OMe}^-] - (n + 1)\log_{10}a_{\mathrm{MeOH}} + \log_{10}(f_{\mathrm{OMe}^-}f_{\mathrm{PhOH}}/f_{\mathrm{PhO}^-})$$

If the anion PhO$^-$ is less solvated for one phenol than another then for the former n will be larger and a higher apparent H_- acidity function for a given sodium methoxide concentration will result. It is relevant that although the ionisation of *o*-t-butylphenol, 2,4-di-t-butylphenol, 2,6-di-t-butylphenol, and 2,4,6-tri-t-butylphenol furnish H_- acidity functions agreeing very well with each other;[1] the slopes of the plots of the four functions against More O'Ferrall and Ridd's H_- scale[12] were 0·78, 0·76, 0·86, and 0·86, respectively. Thus these slopes would suggest that n may be larger for 2,6-di-t-butylphenols than *o*-t-butylphenols as is required if there is a greater steric inhibition to solvation of the anions of the former.

EXPERIMENTAL

The phenols were purified as before[1] and stock solutions in water were prepared.

Sodium hydroxide, sodium hydrogen carbonate, and disodium hydrogen phosphate were all AnalaR, and aqueous solutions of sodium hydroxide were standardised with dried AnalaR sodium carbonate *via* aqueous hydrochloric acid. Buffer solutions containing known concentrations of phenol were prepared and the corresponding pH values were interpolated from the data of Bates and Bower.[2] Complete spectra were recorded using a Unicam S.P. 800 spectrophotometer fitted with a thermostatted (25°) cell compartment. Readings at individual wavelengths were taken from the spectra. Matched 1 cm. (*para, ortho*) or 4 cm. (2, 4) silica cells were used, the blank cell containing buffer solution alone.

The spectra of *p*-t-butylphenol and 2,4-di-t-butylphenol and their anions agreed very well with reported data.[7] The spectral characteristics of *o*-t-butylphenol, which we were unable to find in the literature, were: undissociated *o*-t-butylphenol $\lambda_{\text{max.}} = 270$ mμ ($\varepsilon = 1700$); *o*-t-butylphenoxide anion $\lambda_{\text{max.}} = 240$ mμ ($\varepsilon = 8310$) and 293 mμ ($\varepsilon = 3360$).

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