Spectrophotometric Determination of Basicities of Substituted Naphthoic Acids

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The oasicities of several 6- and 4-substituted 1-naphthoic acids and 6- and 3-substituted 2-naphthoic acids in sulphuric acid media at 30°, are very well correlated by the Hammett equation in all the cases except in the case of 3-substituted 2-naphthoic acids. The methoxy group shows considerable deviation in the Hammett plots. This is attributed to its conjugative interaction with the carboxyl group aided by protonation. Good correlation exists between pK_{BH^+} and σ^+ values in the case of 4-substituted 1-naphthoic acids.

In strongly acid media carboxylic acids undergo protonation either at the carbonyl oxygen or at the hydroxyl oxygen of the carboxyl group. From a study of the protonation in a wide range of sulphuric acid solutions, it is possible to determine accurately the basicities of the acids by applying linear free-energy relationships. The present investigation aims at seeking Hammett correlation with basicity. We have employed sulphuric acid-water mixtures in the protonation since this medium offers an extremely wide and continuous range of acidity, even in dilute aqueous range in which large number of normally neutral compounds are protonated[1].

All the naphthoic acids were prepared by literature methods[2]. Sulphuric acid (E. Merck, AR) was diluted with water and 55-96% (w/w) solutions were prepared.

The procedure reported by us earlier for the determination of pK_{BH^+} was followed[3]. The H_0 values of the acid solutions were taken from the compilation of Paul and Long[4]. Trial experiments indicated that all the naphthoic acids were almost unprotonated upto 55% sulphuric acid solution and almost completely protonated in 96% sulphuric acid solution. The UV absorption spectra of the naphthoic acids in 55% and 96% sulphuric acid solutions were recorded to locate the wavelengths of maximal absorption of the unprotonated (λ_u) and of the protonated (λ_i) forms of the acids. The extinction coefficients in all the solutions were determined at these two wavelengths. The ionization ratio, (I) in each solution was calculated using the equation,

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$$I = \frac{F}{1-F} = \frac{K+CD}{1-K-CD} \qquad \ldots (1)$$

where F is the mol fraction of the ionized form, $D = (\varepsilon)\lambda_i - (\varepsilon)\lambda_u$; $C = 1/[(\varepsilon_i)\lambda_i - (\varepsilon_u)\lambda_i + (\varepsilon_u)\lambda_u - (\varepsilon_i)\lambda_u]$, and $K = C[(\varepsilon_u)\lambda_u - (\varepsilon_u)\lambda_i]$. This method of determining ionization ratio minimises errors due to the effect of change of medium upon absorption and also the errors due to inaccuracies in the concentration of the base[5], since it relies upon differences in absorption at two wavelengths. The pK_{BH^+} values were calculated from the ionization ratios by the method of least squares from the linear Eq. (2). At half-protonation Eq. (2) assumes the form (3) where $H_0^{1/2}$ means the value of acidity function at half-protonation.

$$\log I = mH_0 + C \qquad \ldots (2)$$

$$H_0^{1/2} = -\frac{C}{m} = pK_{BH^+} \qquad \ldots (3)$$

The pK_{BH^+} values measured are presented in Table 1. The thermodynamic significance of the values is known from the realization of linear relation between $\log I$ and H_0 with a slope of almost -1 in all the cases. These values show a regular variation with

Table 1—pK_{BH^+} Values and Logarithm of Molar Extinction Coefficients of Substituted Naphthoic Acids at 30

Substituent	$\log (\varepsilon_u)\lambda_u$	$\log (\varepsilon_i)\lambda_i$	$-pK_{BH^+}$
	1-Naphthoic Acid		
H	4.3006	4.3009	7.30
4-F	4.3087	4.3812	7.35
4-Cl	4.3053	4.3110	7.50
4-Br	4.3117	4.3125	7.50
4-NO₂	4.3166	4.3191	8.10
4-CH₃	4.3121	4.3143	7.05
4-OCH₃	4.2980	4.3015	6.44
6-Cl	4.2895	4.3036	7.40
6-Br	4.3008	4.3053	7.40
6-I	4.2964	4.3003	7.45
6-CH₃	4.2934	4.2793	7.15
6-OCH₃	4.2935	4.3018	7.10
	2-Naphthoic Acid		
H	4.7524	4.7532	7.20
6-F	4.6789	4.6808	7.30
6-Cl	4.6790	4.6808	7.40
6-Br	4.6794	4.6805	7.40
6-CH₃	4.7187	4.7195	7.05
6-OCH₃	4.7015	4.7027	6.70
3-F	4.6848	4.6893	7.45
3-Cl	4.6830	4.6862	7.55
3-Br	4.6835	4.6848	7.60
3-CH₃	4.6920	4.6942	6.97
3-OCH₃	4.6839	4.6853	6.25
Benzoic acid	4.3004	4.3016	7.50

substituents: electron-withdrawing groups decrease and electron-donating groups increase the pK_{BH^+}. The Hammett equation was applied to the data. The Hammett plot for 6-substituted 2-naphthoic acids using the σ_{62} constants[6] gave an excellent correlation ($r = 0.997$; $\rho = 1.46$) for all substituents except the methoxy. Being an electron-donating group, methoxy group is involved in extended conjugation with the protonated carboxyl group, and this may be responsible for the departure of the 6-methoxy group from the Hammett plot. In the absence of σ^+ constants for the 6-substituents in 2-naphthyl system, no further correlation is attempted to improve the situation. In the Hammett plot for 4-substituted 1-naphthoic acids using σ_{41} constants, the methoxy group again shows considerable deviation. However, when the σ^+ constants of Brown and Okamoto[7] are used the methoxy group also fits into the correlation (Fig. 1). The slope of the linear plot is 1.06 with $r = 0.993$. In 4-methoxy-1-naphthoic acid, the methoxy group can assume a preferred orientation *trans* to the adjacent *peri*-H in order to enter into enhanced resonance interaction. The expected decrease in electron-donating power of the methoxy group due to interaction with the acidic medium is compensated by the enhanced resonance of the group and thereby it displays its usual electronic effect as demanded by the σ^+ value.

The pK_{BH^+} values of 6-substituted 1-naphthoic acids are best correlated with σ_p^0 constants. The correlation gives a value of 0.689 for ρ^0 with correlation coefficient 0.970.

The pK_{BH^+} values of 3-substituted 2-naphthoic acids are interpreted as follows. The halogeno substituted acids have low pK_{BH^+} values compared to the parent. The trend in values is as expected from their net electron-withdrawing ability. The high pK_{BH^+} value for the methoxy acid can be attributed to the involvement of methoxy oxygen in stabilising the proton of the conjugate acid through hydrogen bonding.

There is a linear correlation ($r = 0.998$) between the pK_{BH^+} values of 4-substituted 1-naphthoic acids and those of similarly substituted 1-acetonaphthones. A similar correlation exists for 6-substituted 2-naphthoic acids with the corresponding acetonaphthones ($r = 0.997$). Such correlations are indicative of similarity in substituent effects in both the cases.

The data in Table 1 show that 2-naphthoic acid is less acidic than benzoic acid. This means that the 3,4-
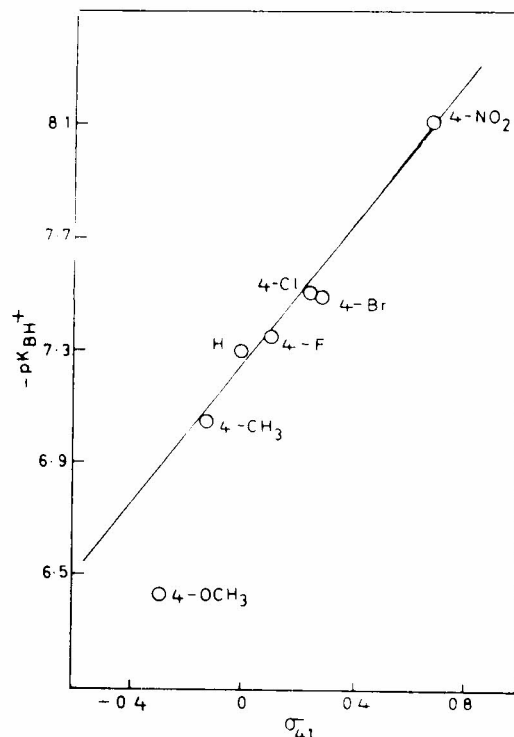

Fig. 1 —Hammett plot for 4-substituted-1-naphthoic acids

benzo group is capable of increasing the electron density at the carbonyl oxygen. This cannot be anticipated from the positive σ value (0.04) of the 3,4-benzo group[8]. However, this is consistent with its reported σ^+ value ($\sigma^+ = -0.13$).

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