

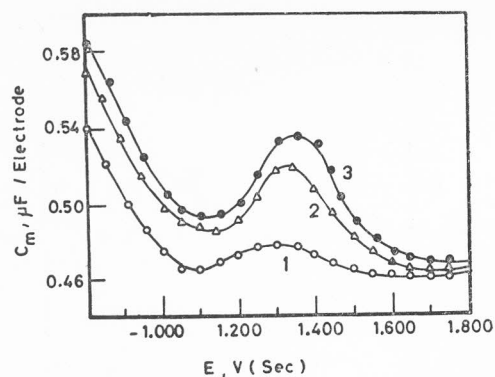


Fig. 1 — Variation of pseudocapacity as a function of polarization for the reduction of Sb(III) in 1M NaOH [Curve 1, [Sb(III)] = 1 mM; curve 2, [Sb(III)] = 2mM; curve 3, [Sb(III)] = 3mM].

R_r and C_r . The method is a direct one and has been shown to lead to quite reliable results⁶. Potentials were measured against a saturated calomel electrode and solutions were de-aerated with purified hydrogen.

According to Grahaime's analysis of the theory of the faradaic admittance⁷, the magnitude of the pseudocapacity peak C_m may be taken as a qualitative measure of the intrinsic speed of the electrode reaction in this medium. The results for the pseudocapacity at 1000 Hz as a function of polarization as obtained during the reduction of trivalent antimony in 1 M NaOH are shown in Fig. 1. Similar curves are obtained in 1 M KOH. In these media, the pseudocapacities appear as humps and shift slightly towards more negative potentials with increase in antimony concentration. C_m tends to increase in magnitude with increase in [Sb(III)]. The half wave potential for the reduction of trivalent antimony to the metal is -1.255 and -1.260 V in 1 M NaOH and 1 M KOH respectively, in agreement with the already reported value in 1 M NaOH⁸.

The specific rate constant for the exchange Sb(III)/Sb(Hg) was calculated following the simple model of the faradaic impedance⁹. According to this model,

$$R_r - 1/\omega C_r = \frac{RT}{n^2 f^2 AC} \cdot \frac{1}{k_s}$$

where k_s is the standard rate constant in cm sec⁻¹, C the concentration in g ion/cm³, A the area in cm², n the number of electrons involved in the reduction, R_r and C_r are respectively the resistive and capacitive components of the faradaic admittance. The various quantities involved in the calculation together with the calculated k_s values at 25°C in 1 M NaOH are shown in Table 1. Similar results are obtained in 1 M KOH. The rate constant for the reduction of trivalent antimony is the same in the two media being $\sim 3.3 \times 10^{-4}$ cm/sec.

The values of k_s at different temperatures in 1 M NaOH show that k_s increases with increase in temperature. By plotting log k_s against 1/T an approximate straight line is obtained. The energy of activation as obtained from the slope is 4.8 ± 0.5

TABLE 1 — APPARENT STANDARD RATE CONSTANT (k_s) OF THE EXCHANGE Sb(III) + 3e $\rightleftharpoons$ Sb(Hg) in 1 M NaOH AT 25°C

$$[A=0.0300, R_s=40, C_d=0.45]$$

C(mM)	Freq. (Hz)	C_m	R_m	R_r	$\frac{1}{\omega C_r}$	$k_s \times 10^4$
1.0	1000	0.480	84	3271	270	3.3
	3000	0.470	51	3123	29	3.3
2.0	1000	0.498	105	1600	80	3.3
	3000	0.484	51	1579	80	3.3
3.0	1000	0.526	130	1029	29	3.3
	3000	0.474	50	1025	28	3.3

kcal. From the values of reaction rate constants at different temperatures, it may be concluded that reduction of Sb(III) under these experimental conditions is irreversible¹⁰.

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Spectrophotometric Determination of Basicities of Substituted Acetonaphthones

P. ANANTHAKRISHNA NADAR*† & G. VARGHESEDHARUMARAJ
Postgraduate Department of Chemistry, V. H. N. S. N. College,
Virudhunagar 626 002

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The basicities of several 6-substituted 2-acetonaphthones and of 4-substituted 1-acetonaphthones have been determined spectrophotometrically in sulphuric acid media at 30°. The Hammett equation has been applied in both series. The point for the methoxy group deviates considerably from the Hammett plot in both the series. A very good linear correlation exists between pK_{BH^+} and σ_p^+ in the case of 4-substituted 1-acetonaphthones.

THE linear free-energy relationships are successful in correlating reactivities of many side-chain reactions in benzene derivatives¹. The applicability of these relationships to naphthalene derivatives has been tested in only a few cases²⁻⁷. The basicities of several 6-substituted 2-acetonaphthones and 4-substituted 1-acetonaphthones have now been deter-

*Present address: Perarignar Anna University of Technology, Madras 600025.

mined employing spectrophotometric method in sulphuric acid solution. The Hammett relation has been applied to the data obtained.

All the substituted acetophenones were prepared as described in literature^{8,9} and their purity ascertained by TLC. Sulphuric acid (E. Merck, AR) was diluted with water and solutions ranging from 45 to 95% (w/w) were prepared.

Measurement of pK_{BH^+} — A weighed sample of each ketone was dissolved in 85% sulphuric acid-water (w/w) to give a 5.0×10^{-4} M-stock solution, from which 1 ml aliquots were pipetted into 10 ml volumetric flasks and made up to volume with suitable sulphuric acid-water mixtures so as to give solutions of desired acid concentrations. The final concentration of the acid in all the solutions was determined by titration against standard alkali. The H_0 values of the acid solutions were taken from the compilation of Paul and Long¹⁰. A trial experiment indicated that 45% sulphuric acid could be chosen as the reference solvent for the unprotonated form and 95% sulphuric acid as the reference solvent for the protonated form of the ketones. The solutions were equilibrated at 30° and transferred to a quartz cell of 1 cm path length and the maximum absorption recorded on a Perkin-Elmer Hitachi-200 UV-Vis spectrophotometer. The UV spectra of the ketones in 45% and 95% acid were recorded. The results are given in Table 1. The pK_{BH^+} values were obtained by the method of Davis and Geissman¹¹. The difference $[\epsilon_{\lambda_1} - \epsilon_{\lambda_u}]$ was plotted against H_0 (where λ_1 and λ_u represent maximum absorption for protonated and unprotonated forms of ketones respectively). The extinction coefficients measured in various acid solutions for 1-acetophenone are given in Table 2.

The values of pK_{BH^+} (Table 1) show a regular variation with substituents: electron-withdrawing groups decrease and electron-donating groups

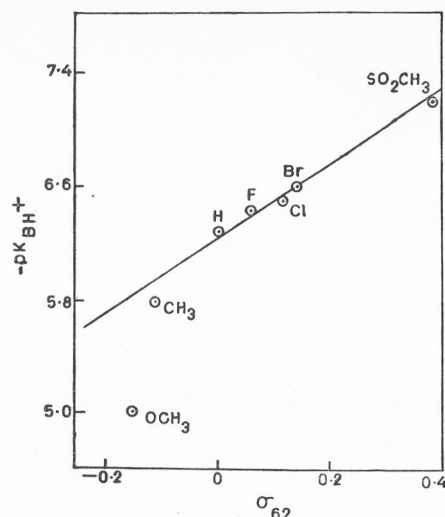


Fig. 1 — Hammett plot for 6-substituted 2-acetonaphthones

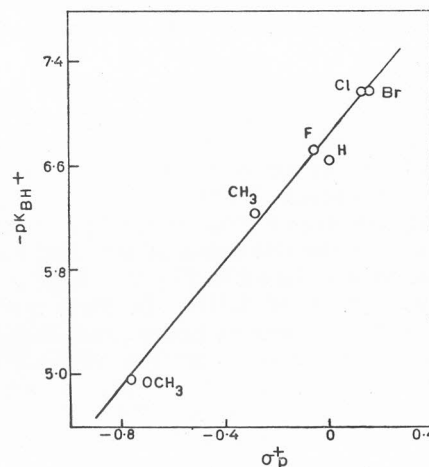


Fig. 2 — pK_{BH^+} versus σ_p^+ plot for 4-substituted 1-acetonaphthones

TABLE 1 — pK_{BH^+} VALUES AND WAVELENGTH MAXIMA FOR SUBSTITUTED ACETONAPHTHONES AT 30°

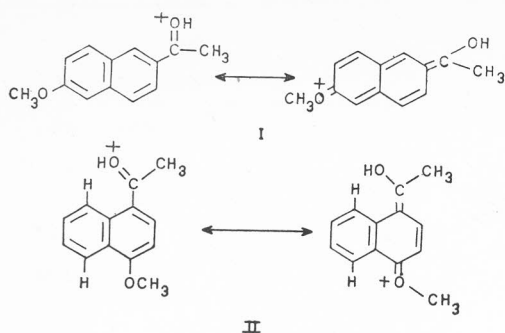
Substituent	$-pK_{BH^+}$	λ_{max} (nm) in	
		45% H_2SO_4	95% H_2SO_4
6-SUBSTITUTED 2-ACETONAPHTHONES			
H	6.3	250	272
F	6.4	250	274
Cl	6.5	230	273
Br	6.6	240	271
SO_2CH_3	7.2	232	315
CH_3	5.8	255	278
OCH_3	5.0	240	272
4-SUBSTITUTED 1-ACETONAPHTHONES			
H	6.7	246	274
F	6.8	246	271
Cl	7.2	252	290
Br	7.2	254	273
CH_3	6.3	251	278
OCH_3	5.0	249	302
Acetophenone	6.8	250	290

Values are accurate to ± 0.05 unit.

increase the pK_{BH^+} . The Hammett equation was applied to the data. the Hammett plot (Fig.1 for 6-substituted 2-acetonaphthones) using the σ_{62} constants evaluated from saponification of methyl naphthoates¹² gave an excellent correlation ($r = 0.999$; $\rho = 2.63$) for all substituents except the methoxy.

TABLE 2 — ABSORPTION MAXIMA AND EXTINCTION COEFFICIENTS FOR 1-ACETONAPHTHONE

$H_2SO_4\%$	$\epsilon_i(274nm)$	$\epsilon_u(246nm)$	$(\epsilon_i - \epsilon_u)$	$-H_0$
45	2500	13789	-11289	2.85
50	2723	14646	-11923	3.38
55	2731	14662	-11931	3.91
60	2606	14432	-11826	5.46
65	1869	12944	-11075	5.04
70	2762	12526	-9764	5.65
75	3501	9978	-6477	6.30
80	9784	8247	1537	6.97
85	12784	5273	7511	7.66
90	13408	3407	10001	8.27
95	15057	4826	10231	8.86



Being an electron-donating group, methoxy group is involved in extended conjugation with the protonated carbonyl group as illustrated in (I).

This type of direct resonance may be responsible for the departure of the group from the Hammett plot. In the absence of σ^+ constants for the 6-substituents in the 2-naphthyl system, no further correlation is attempted to improve the situation.

In the Hammett plot for 4-substituted 1-acetonaphthones using σ_{41} constants evaluated from ester hydrolysis, the methoxy group, except for other substituents ($r = 0.99$; $\rho = 2.33$ of 30°), shows considerable deviation. However, when the σ_p^+ constants of Brown and Okamoto¹³ are used, the methoxy group also fits into the correlaton (Fig. 2). The slope of the line is 2.41 with $r = 0.987$. In 4-methoxy-1-acetonaphthone, the methoxy group can assume a preferred orientation *trans* to the adjacent *peri*-H in order to enter into enhanced resonance interaction¹⁴ with the carbonyl group as illustrated in (II). The expected decrease in electron-donating power of the group due to interaction with the acidic medium will be compensated by the enhanced resonance of the group and thereby it can display its usual electronic effect as demanded by the σ^+ value.

The data in Table 1 indicate that 2-acetonaphthone is more basic than acetophenone. This means that the 3,4-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 group¹⁵. However, this is consistent with its reported σ^+ value¹⁶ ($\sigma^+ = -0.13$). It is seen that 1-acetonaphthone is less basic than 2-acetonaphthone. This may be due to the presence of the *peri*-H in 1-acetonaphthone which forces the carbonyl group out of the naphthalene plane and inhibits the resonance between the ring and the carbonyl group thereby decreasing the electron density at the carbonyl oxygen compared to that in 2-acetonaphthone in which such inhibition of resonance is absent.

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pH & Spectral Studies on Some Azo Compounds

MAMDOUH S. MASOUD*, T. M. SALEM & M. HINNAWI
Chemistry Department, Faculty of Science, University of Alexandria, Alexandria, Egypt

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pH and spectral studies on 2-carboxyphenylazo- β -naphthylamine, 2,4-dihydroxyphenylazo-2'-hydroxybenzene and 1-(2-pyridylazo)-2-naphthol have been carried out. Solvents of different polarities have been used for electronic spectral measurements to study the possible species formed. pK values for these compounds are also reported.

WE report here the results of our pH and spectral measurement studies on 2-carboxyphenylazo- β -naphthylamine (CPANA), 2,4-dihydroxyphenylazo-2'-hydroxybenzene (DPAHB) and 1-(2-pyridylazo)-2-naphthol (PAN). We have undertaken these studies with a view to identifying the chromophoric species, to calculate the pK values and relate these to the molecular structures of the dyes.

2-Carboxyphenylazo- β -naphthylamine (CPANA) and 2,4-dihydroxyphenylazo-2'-hydroxybenzene (DPAHB) were prepared following standard procedure¹ while 1-(2-pyridylazo)-2'-naphthol (PAN) was a B.D.H. reagent of high purity.

A Radiometer 28 pH meter was used to measure the pH values during the course of titrations. Unicam SP800 spectrophotometer was used for measuring the electronic spectra. Unicam SP200 and Unicam SP1200 spectrophotometers were used for recording the IR spectra.