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THE BASICITIES OF SOME AROMATIC SULPHOXIDES IN AQUEOUS SULPHURIC ACID BY U.V. MEASUREMENTS.

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Following preliminary research work on some aromatic sulphoxides (1) it has been considered of interest - beside kinetic measurements - to determine the basicity of such molecules in aqueous sulphuric acid by the u.v. spectrophotometric method . Basicity data available on sulphoxides in sulphuric acid (2) are, in fact , rather few or limited to non aqueous solvents (3) .

When the protonation extent of sulphoxides is determined by following variations of spectroscopic feature of the free base and protonated form, the absorption bands of the present species are modified in such a way that some inconvenience to the analytical method arises.

A solvent effect on absorption maxima, a relative uncertainty in ε_B and ε_{BH^+} values beside appreciable variations in pK values depending on the choice of wavelength , has been observed.

The use of several calculation methods and also the introduction of proper corrections in order to obtain pK values (4,5,6) has been tested by us.

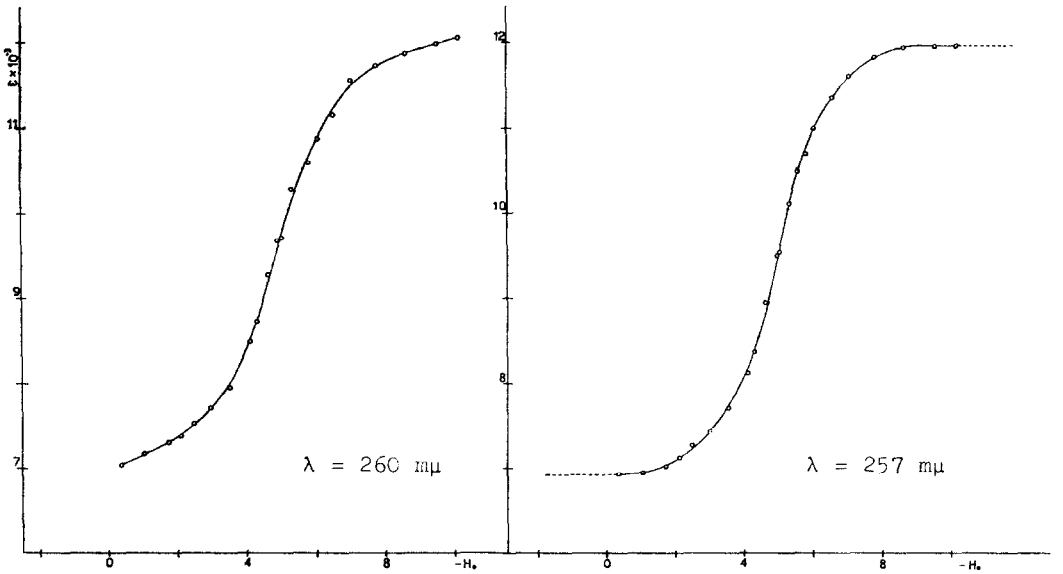
Besides approximations already known , in the course of this work a criterion has been elaborated by us which tends to confine arbitrary assumptions related to the choice of the λ and based on the analysis of the absorption features within the whole range of acidity examined (from 1% to 94%).

For the molecules studied, besides absorption band modifications, a progressive shift of absorption maxima increasing acid strength has been observed ; more precisely , a shift towards shorter wavelengths,then constant behaviour followed by a shift towards longer wavelengths does occur.

Since the medium effect should have the same weight on the two species present in the inversion region, the choice of the λ in that range for pK calculations does seem reasonable.

In Table I the sulphoxides examined in the present work together with the wavelength choosen for each of them, following the approximation indicated by us, are reported. To the corresponding ε values calculation methods have been applied on the base of sigmoid type curves obtained by plotting ε against H_o , and straight lines by plotting $\log \frac{\varepsilon_{BH^+} - \varepsilon}{\varepsilon - \varepsilon_B}$ against H_o . In the first case good titration curves sufficiently flat both at low and high acidity regions have been obtained; extrapolation for the ε_B and ε_{BH^+} values to be utilized in the second case , was possible.

The advantages deriving from the use of this method are mainly based on the fact that itself is not bound to the existence of an isosbestic point (7) not always well identifiable , or to uncertainty of the right λ value corresponding to 50% protonation (5), strictly dependent on the wavelength initially choosen. Moreover the influence on ε values by a shift of each absorption curve in this region is less marked compared with the case of choice of wavelength in the range of highest spectral difference between free base and protonated form. Fig. 1 does show the behaviour observed in both cases.



λ in highest spectral difference λ selected in the present work

Fig. 1 : p-NITRO-METHYLPHENYLSULPHOXIDE

TABLE I

COMPOUNDS[a]	H_o at ½ prot.[b]	m[c]	H_o at ½ prot.[d]	m[d']	pK_a[d"]	Ø[e]	pK_a[e]	l[f]	N°[g]
$H_3CSOC_6H_4CH_3(p)$	-3.28	0.516	-3.25	0.521	-1.72	0.541	-2.08	219	12
$H_3CSOC_6H_5$	-3.68	0.503	-3.70	0.519	-1.92	0.575	-2.26	214	15
$H_3CSOC_6H_4NO_2(m)$	-4.06	0.631	-4.07	0.666	-2.71	0.355	-3.07	213	9
$H_3CSOC_6H_4NO_2(p)$	-4.93	0.580	-4.87	0.574	-2.80	0.466	-3.20	257	14
$H_5C_6SOC_6H_4CH_3(p)$	-4.64	0.492	-4.54	0.492	-2.23	0.552	-2.72	235	13
$H_5C_6SOC_6H_5$	-5.16	0.461	-5.24	0.455	-2.39	0.612	-2.85	229	11
$H_5C_6SOC_6H_4NO_2(m)$	-5.72	0.523	-5.60	0.531	-2.97	0.515	-3.41	248	11
$H_5C_6SOC_6H_4NO_2(p)$	-5.81	-	-5.86	0.522	-3.05	0.521	-3.50	265	14

a) Data obtained at 25°C.

b) From sigmoid graph of ϵ against H_o values indicated by Jorgenson and Hartter.

c) From sigmoid graph by methods of A.R.Katritzky, A.J.Waring and K.Yates, Tetrahedron, 19, 465, (1963).

d) By least squares from straight lines, d') slopes, d") intercepts. By methods of K.Yates.

e) By methods of J.F.Bunnett.

f) At inversion point of absorption maxima.

g) Number of points between 5-95% of protonation used to determine m and pK_a by least squares.

The Table I gives also the pK values calculated by these methods, together with the slopes and intercepts of straight lines obtained.

The results, herewith illustrated, do point out that sulphoxides cannot be regarded as Hammett bases ; in all cases considered, straight lines with slopes very far from unity have been obtained . Therefore the pK values so derived are simply equal numerically to the H_0 at half-protonation values, but do not represent the thermodynamic equilibrium constants .

In order to establish the latters, two independent approximations, respectively indicated by K.Yates (8) and J.F.Bunnett (9) , have been used, and results are given in Table I.

Work is actually in progress in order to investigate differences in pK_a values either using Yates or Bunnett methods, as far as the protonation site in sulphoxide group is concerned.

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