A Novel Method of Measuring the Protonation of Sulphoxides

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Summary The amplitude of the shorter wavelength dichroic extremum of optically active phenyl alkyl sulphoxides depends on the degree of protonation of the SO group and may be used to evaluate their pK_a.

THE measurement of the pK_a of sulphoxides in water, by evaluation of the protonation ratio† [SOH$^+$]/[SO] from u.v. and n.m.r. data,[1] has some limitations. The n.m.r. method[1,2] is applied easily only to alkyl sulphoxides having α-C–H bond. The u.v. method is more general,[1] but the change of optical density with protonation is complicated by strong solvent effects on the absorption of free base and conjugated acid.

Searching for alternative methods, we observed that the circular dichroism (c.d.) spectrum‡ in water of (+)-t-butyl phenyl sulphoxide§ presents, beside the well known[3]

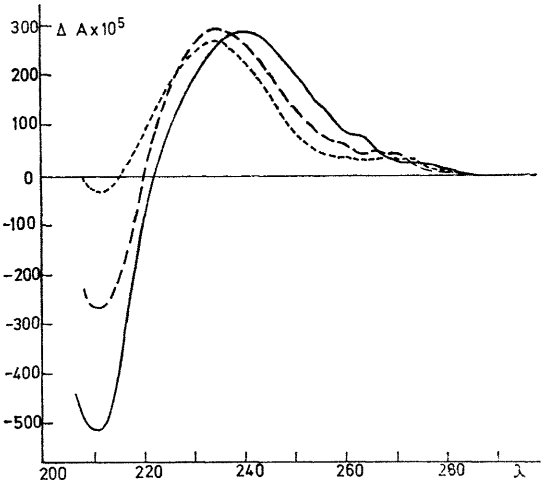

FIGURE 1. *Effect of acidity of the medium on the c.d. spectra of* (+)*-t-butyl phenyl sulphoxide* (1·08 × 10^{-4}M): —— *in water*; — — *in* HClO$_4$ 6·12M; - - *in* HClO$_4$ 10·4M.

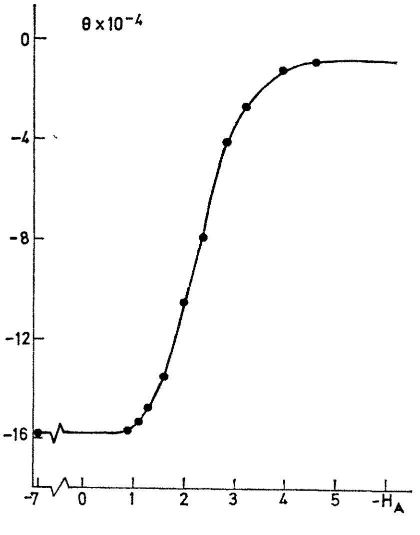

FIGURE 2. *Relationship between molecular ellipticities* (θ) *and* —H$_A$, *for the dichroic extremum at* 210 nm *of* (+) *t-butyl phenyl sulphoxide.*

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† [SOH$^+$] and [SO] are the concentrations of the sulphoxide in the protonated and free base form, respectively.

‡ All c.d. spectra were taken on a Roussel–Jouan 185 Model II Dichrograph.

§ Prepared following Andersen's method (K. K. Andersen, W. Gaffield, N. E. Papanikolaou, J. W. Foley, and R. I. Perkins, *J. Amer. Chem. Soc.*, 1964, **86**, 5637); Ph-SO-Bu^t[α]$_D$ + 182° (*c* 1 in 95% EtOH), m.p. 89—90°; Ph-SO-Pr^i [α]$_D$ + 170° (*c* 1 in Me$_2$CO); b.p. 101—102° at 0·01 mm Hg.

positive band at *ca.* 240 nm, a negative dichroic extremum at 210 nm.

Whereas the positive band at 240 nm is only slightly affected by the acidity of the medium, the negative extremum at 210 nm decreases in intensity with the degree of protonation of the SO group (Figure 1). Our finding proved to be useful in evaluating the pK_a of sulphoxides.

The decrease of molecular ellipticity with acid concentration is not due to a solvent effect, since no changes are observed in the spectrum in going from water to 2·08M-$HClO_4$ ($H_A = - 0{\cdot}88$)¶, but to the protonation of the SO group.

A plot of the molecular ellipticities, measured for various perchloric acid solutions of (+)-t-butyl phenyl sulphoxide, *vs.* $-H_A$, the acidity function obeyed by sulphoxides,[1,4] gives a typical sigmoid curve (Figure 2). From these measurements the pK_a of the sulphoxide was evaluated. The result (p$K_a = - 2{\cdot}3$) is in fair agreement with that (p$K_a = - 2{\cdot}19$) obtained from u.v. measurements.[5]

This technique was also tested with (+)-isopropyl phenyl sulphoxide,§ whose pK_a has been measured satisfactorily by u.v. and n.m.r. methods,[6] (pK_a = − 2·35, − 2·56, and − 2·56 by c.d., u.v., and n.m.r. methods, respectively). The method can probably be adopted for other optically active substrates and research is in progress along these lines.

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¶ For use of the acidity function H_A see refs. 1 and 4

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