Solvent Effects in the Nuclear Magnetic Resonance Spectra of Organic Acids and Salts

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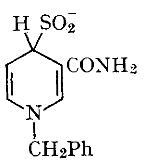
DURING studies on the intermediate in the dithionite reduction of pyridinium salts, we measured the n.m.r. spectrum of compound (I) in deuterium oxide and $(CD_3)_2SO$. The chemical shift of the proton at C-4, α to the sulphinate group, is solvent dependent. In D_2O, the signal is centred at δ = 231 c./sec., whereas in (10%) 1N-NaOH in $(CD_3)_2SO$ it appears at 205 c./sec.[1] In this Communication we present the results of a more general study using simpler acids and their sodium salts, in particular butyric acid, n-butylsulphinic acid, and n-butylsulphonic acid.



(I)

For all the salts, the change from D_2O to $(CD_3)_2SO$ results in a shift of δ to higher fields for the signal of the α-CH_2. The chemical shifts of the β, γ, and δ protons vary only slightly with the solvent. The change of δ of the α-CH_2 may be explained by an increase in effective charge on the anion which is strongly solvated in water but essentially free in $(CD_3)_2SO$.[3] This effect is greater for the salts of sulphonic and sulphinic acids than for those of carboxylic acids.

For butyric acid, when comparing the results obtained for the salt with those for the acid, we observe a change in δ of 11 c./sec., in agreement with published results.[4] The change from D_2O to $(CD_3)_2SO$ results in only a slight change in δ for the CH_2, α to the carboxyl group. This is in accord with limited dissociation of the acid in water, as well as in $(CD_3)_2SO$.[2]

The strongly acidic n-butylsulphonic acid is completely dissociated in water. Only a very slight change in δ for the α-CH_2 occurs on going from solutions of the salt to those of the acid. Butylsulphonic acid is not completely dissociated in $(CD_3)_2SO$ solution: it is found that the signal corresponding to the α-CH_2 is at lower field for the acid than for the salt.

The above results are consistent with the increase in pK_a values of acids whose anions have localised charges when the solvent is changed from water to Me_2SO.[5]

n-Butylsulphinic acid is a relatively weak acid

TABLE

Nuclear magnetic resonance data†

		γ-CH_3	β-CH_2	α-CH_2
n-Butyric acid	D_2O	49	89	134
sodium salt	D_2O	47	87	123
n-Butyric acid	$(CD_3)_2SO$	51	90	130
sodium salt	$(CD_3)_2SO$	48	85	111

		δ-CH_3	β-CH_2 + γ-CH_2	α-CH_2
n-Butylsulphonic acid	D_2O	49	*ca.* 90	170
sodium salt	D_2O	51	*ca.* 90	172
n-Butylsulphonic acid	$(CD_3)_2SO$	50	*ca.* 86	160
sodium salt	$(CD_3)_2SO$	49	*ca.* 84	146
n-Butylsulphinic acid	D_2O	49	*ca.* 85	163
sodium salt	D_2O	49	*ca.* 85	138
n-Butylsulphinic acid	$(CD_3)_2SO$	51	*ca.* 85	154
sodium salt	$(CD_3)_2SO$	50	*ca.* 82	111

† Measured on a Varian A–60 spectrometer; chemical shifts (δ) in c./sec.; concentrations: 5% by weight. [Spectra taken at greater or lesser dilution (2—10%) show negligible variation in chemical shifts.] Internal references: in D_2O: sodium trimethylsilylpropanesulphonate; in $(CD_3)_2SO$: $(CD_3)(CD_2H)SO$.

(benzenesulphinic acid: $pK_a = 1{\cdot}5$[6]). Assuming a pK_a of the same order of magnitude, n-butylsulphinic acid is weakly dissociated in aqueous solution, which explains the change in δ for the α-CH_2 on comparing the salt with the acid. The pK_a of the acid in $(CD_3)_2SO$ solution is unknown; however our measurements suggest that ionisation is incomplete: it is found that δ for the α-CH_2 is at higher field for the salt than for the acid.

This solvent effect on the α-methylene of the salts and of the acid may be used for the identification of this group and for study of the behaviour of this compound in different solvents.

(*Received, March* 16*th*, 1967; *Com.* 255.)

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