Site of Protonation in Sulphoxides: Carbon-13 Nuclear Magnetic Resonance Evidence

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Summary ^{13}C n.m.r. results show that the protonation of sulphoxides occurs at oxygen, rather than at sulphur.

WHEN different basic centres are present in the same molecule and particularly when they are part of the same chemical function, contradictory data have often been obtained about the site of protonation.[1] In sulphoxides (R_2SO), protonation at oxygen is suggested by i.r. data[2] and acid-base equilibria studies,[3] while ^{1}H n.m.r. data[4] have been interpreted as evidence for protonation at sulphur.

The resonance of the acidic proton, which shows up as a singlet at low temperature in FSO_3H–SbF_5–SO_2ClF, occurs in protonated dimethylsulphoxide (DMSO) at δ 6·83 p.p.m.,[4] in the same range as the acidic proton of the conjugate acid of dimethylsulphide (δ 6·52 p.p.m. heptuplet).[5] The chemical shift evidence was however considered to be tenuous[6,7] particularly because in the spectra of protonated DMSO no coupling between the acidic proton and the hydrogens linked to the α carbons could be detected, whereas in the case of sulphides a coupling constant of *ca.* 8 Hz was observed.[5]

We measured the ^{13}C chemical shift† of several weak bases, whose protonation site is unambiguous, as well as those of DMSO and diethyl sulphoxide (DESO), in dilute

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† The Fourier transform ^{13}C n.m.r. spectra were run on a Bruker HFX/10 spectrometer at room temperature, using solutions 10—15% by vol. The Me_3NH^+ ion was used as internal standard to minimize solvent effects.[3]

TABLE. ^{13}C *Chemical shifts of weak bases in sulphuric acid solutions and in trifluoroacetic acid*[a]

			δ (p.p.m.)[a]			Δδ[b]		
Base	X	$[H_2SO_4]$ (M)	Me	CH_2	CO	Me	CH_2	CO
Me–X–Me	O	18	−16·6	—	—	−1·8	—	—
		0·9	−14·8	—	—			
	CO	18	+15·3	—	−197·4	+0·9	—	−27·9
		0·9	+14·4	—	−169·5			
	SO	18	+11·2	—	—	+5·0	—	—
		0·9	+ 6·2	—				
$Me–CH_2–X–CH_2–Me$	O	18	+34·0	−30·8	—	+2·7	—9·5	—
		0·9	+31·3	−21·3	—			
	S[c]	18	+35·3	+16·5	—	+0·8	−1·2	—
		12·2[c]	+34·5	+17·7	—			
	CO	18	+38·5	+ 9·6	−204·0	+1·1	0	−28·0
		0·9	+37·4	+ 9·6	−176·0			
	SO	18	+39·9	+ 4·2	—	+1·3	+2·9	—
		0·9	+38·6	+ 1·3	—			
$Me_3\overset{+}{S}{=}OBF_4^-$		CF_3COOH	+ 5·9	—	—	−0·3[d]		
$Me_2S{=}\overset{+}{O}MeBF_4^-$		CF_3COOH	+12·5[e]	—	—	+6·3[d]		
Me_2SO		CF_3COOH	+ 8·6	—	—	+2·4[d]		

[a] At room temperature, Me_3NH^+ used as internal standard; [b] $\Delta\delta = \delta_{conc} - \delta_{dil}$; [c] the poor solubility of the sulphide in dilute acid forced us to measure the chemical shift in 12·2M H_2SO_4 where the substrate is substantially protonated; [d] $\Delta\delta = \delta_{CF_3COOH} - \delta_{H_2SO_4 dil}$; [e] this is the chemical shift of the two equivalent methyl groups linked to the sulphur; the resonance of the OMe group is 17·6 p.p.m. downfield from the internal standard.

and concentrated acid solutions (see Table), in order to determine the spectra of both the free base and the conjugate acid. In the concentrated acid, the extent of protonation was not always complete and varied because of the different basic properties of ethers,[8] sulphides,[9] ketones,[10] and sulphoxides.[3] The degree of protonation is expected to affect the magnitude but not the direction of the chemical shift.

The data on ethers, sulphides, and ketones indicate that protonation causes a downfield shift in the resonance of the carbon α to the protonation site,‡ whereas the resonance of the β and γ carbons are shifted in the opposite direction.

The spectra of DMSO and DESO show that both the methyl and methylene carbon resonances are shifted to higher fields as a result of protonation. Ketones show a similar shift but sulphides and ethers do not. This suggests that the carbons in the sulphoxides are not α to the protonation site, which must therefore be oxygen.

To confirm this hypothesis, the spectra of $Me_3\overset{+}{S}OBF_4^-$, (I), (a model for sulphur protonated DMSO) and or $Me_2\overset{+}{S}OCH_3BF_4^-$, (II), (a model for oxygen protonated DMSO) have been recorded in trifluoroacetic acid and compared with those of DMSO (see Table).§ The results are in agreement with those discussed above since the carbon resonance of the three equivalent methyls of (I) are downfield with respect to DMSO in the same solvent and in water, whereas the carbon resonance of the two equivalent methyls of (II) are upfield.

A general explanation of the effect of protonation on ^{13}C chemical shifts of these and others compounds[12,13] needs further theoretical and experimental work. Nevertheless, the results reported above are quite clear evidence that oxygen is the protonation site in sulphoxides.

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‡ In the case of ketones the carbonyl carbon is therefore referred to as the α carbon.

§ Compounds (I) and (II) have been synthesized following a procedure similar to that described for the corresponding perchlorates.[1]

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