The Use of Nuclear Magnetic Double Resonance to Detect and Characterise Phenolic OH Groups

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COMMERCIAL supplies of deuterochloroform (a common solvent for studies of proton magnetic resonance spectra) contain small quantities of water which gives rise to an n.m.r. absorption band

at 1·5 p.p.m. to low fields of an internal tetramethylsilane (TMS) reference. This water impurity can be used to one's advantage in conjunction with double resonance equipment to identify absorption bands from groups which undergo slow reversible chemical exchange with water.

Figure 1a shows the ^{1}H resonance spectrum of 2,4,6-trichlorophenol at 100 Mc./sec. observed under conditions of frequency sweep. The small water absorption band (probably due to DOH) appears at 1·50 p.p.m. to low field of tetramethylsilane and is not shown on the spectrum. Figure 1b shows the spectrum obtained when the water absorption is irradiated in a double-irradiation frequency-swept experiment. The band assigned to the phenolic OH protons disappears: this is because saturated protons in the water molecules are chemically exchanged with the phenolic OH protons.[1]

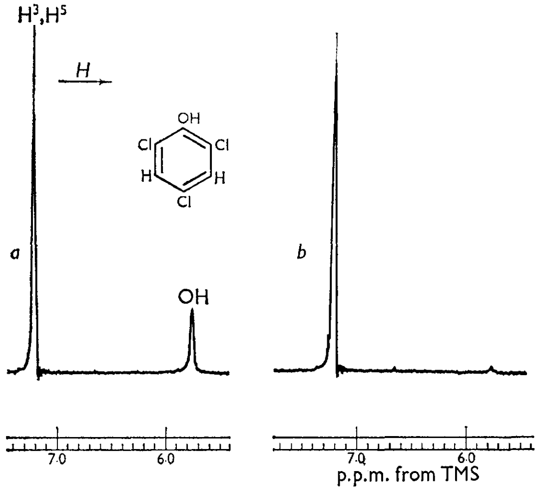

FIGURE 1: *The ^{1}H resonance frequency-swept spectrum at 100 Mc./sec. of 2,4,6-trichlorophenol in* $CDCl_3$ *solution.*
(*a*) *With no double irradiation.*
(*b*) *With strong irradiation at the* DOH *frequency* (1·50 *p.p.m. from TMS*).

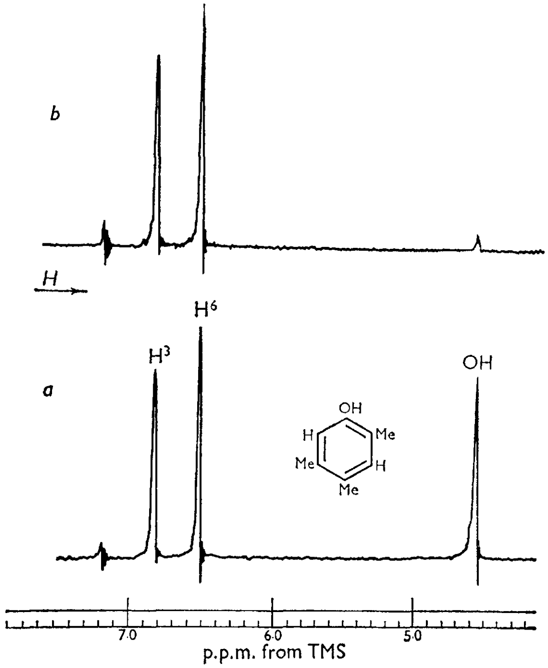

FIGURE 2: *The* ^{1}H *resonance frequency-swept spectrum at 100 Mc./sec.* of *2,4,5-trimethylphenol in* $CDCl_3$ *solution.*
(*a*) *With no double irradiation.*
(*b*) *With strong irradiation at the* DOH *frequency* (1·73 *p.p.m. from TMS*).

TABLE

Compound	Chemical shift of irradiated DOH band δ (p.p.m.)[a]	Collapse of phenolic OH peak
(1) 4-Chlororesorcinol	1·60	Complete
(2) 4,5-Dimethoxyresorcinol	1·53	Complete
(3) *m*-Hydroxybenzaldehyde	1·20	Complete
(4) Catechol	1·30	Complete
(5) Pyrogallol	1·52	Complete
(6) 2,4,6-Trichlorophenol	1·50	Complete
(7) 2,4,5-Trimethylphenol	1·73	Complete
(8) 2-Acetyl-3-methoxyphenol	1·75	Slightly (*ca* 15%) (OH chelated)
(9) 1-Naphthol	1·65	Complete
(10) 3-Chlorosalicyclic acid[b]	1·62	Complete

[a] δ measured in p.p.m. to low fields of TMS internal reference.
[b] The CO_2H absorption band also shows partial collapse.

Figure 2 shows the results of a similar experiment on 2,4,5-trimethylphenol. Using this method on the phenols listed in Table 1, it was possible to either remove the OH absorption band or to reduce its intensity in all cases. When the phenolic OH is chelated it is possible only partially to reduce the OH intensity by this method.

The method works most effectively for dilute solutions where the ratio of water to compound is higher. For aliphatic alcohols and carboxylic acids the exchange between the water and the OH or CO_2H groups is often such that two separate absorption bands are not observed and in such cases the method cannot be used. A further complication in the case of aliphatic alcohols is that dilute solutions of the latter have their OH absorption at high fields close to where one would expect the water band: this makes the double resonance experiment difficult to carry out. However, for phenolic OH groups the double resonance technique offers a useful and rapid method of detecting the OH absorption band.

The measurements were made with a Varian HA-100 spectrometer.

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[1] S. Forsén and R. A. Hoffman, *J. Chem. Phys.*, 1963, **39**, 2892.