The Nuclear Magnetic Resonance Spectrum of $H_2{}^{18}O$ in Dioxan–$CDCl_3$ Solutions

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Summary The chemical shift of a dilute $H_2{}^{18}O$ solution is *ca.* 0·3 p.p.m. lower than that of $H_2{}^{16}O$.

IT has recently been shown that the n.m.r. signal of the acetonitrile protons, hydrogen-bonded to the oxygen atoms of $H_2{}^{18}O$ molecules, appears 12 Hz higher than in the corresponding $H_2{}^{16}O$ case.[1] Although this observation falls in line with a large number of similar anomalous phenomena peculiar to ^{18}O-compounds[1] this appreciable difference in the chemical shift of a proton as a result of exchanging its hydrogen bonding oxygen-16 atom for an oxygen-18 atom cannot as yet be explained on basis of the existing theories. It therefore seemed interesting to compare the chemical shift of a proton *covalently* bonded to an oxygen-18 atom with that of a similar proton bonded to an oxygen-16 atom. The n.m.r. spectrum of very dilute solutions of $H_2{}^{18}O$ in dioxan–$CDCl_3$ was therefore compared with that of the corresponding $H_2{}^{16}O$ solutions in order to investigate the signals of monomeric, rather than trimeric or polymeric, water modifications. Under these conditions the H_2O molecules are no doubt hydrogen-bonded to the dioxan oxygen atoms. The Table gives the results obtained in these measurements carried out with a 100 MHz Varian HA spectrometer, using the side-band technique (lock signal: $SiMe_4$; temperature: 28°; sweep time of 1000 Hz: 250 sec.).

The observed 366—370 Hz signal belongs no doubt to the dioxan protons since a CCl_4 solution of dioxan was found to show an n.m.r. signal at 3·57 p.p.m., relative to $SiMe_4$, corresponding in our case to *ca.* 360 Hz.[2]

The downfield chemical shifts (Hz) observed for $H_2{}^{16}O$ *and* $H_2{}^{18}O$ *solutions in dioxan*–$CDCl_3$

	Solution		
(I)	0·1 ml $H_2{}^{16}O$ + 10 ml dry dioxan, diluted 1 : 4 in $CDCl_3$	244[a]	366
(II)	0·1 ml 97·6% $H_2{}^{18}O$ (normalized with respect to its H/D ratio) + 10 ml dioxan, diluted 1 : 4 in $CDCl_3$	211	369
(III)	0·02 ml $H_2{}^{16}O$ + 10 ml dioxan, diluted 1 : 4 in $CDCl_3$	234	366
(IV)	0·02 ml 97·6% $H_2{}^{18}O$ (+0·49% $H_2{}^{17}O$) +10 ml dioxan, diluted 1 : 4 in $CDCl_3$ ..	222	367
(V)	0·03 ml 46·3% $H_2{}^{18}O$ (+15·4% $H_2{}^{17}O$) +20 ml dioxan, diluted 1 : 9 in $CDCl_3$ ..	208	368
(VI)	0·2 ml 46·3% $H_2{}^{18}O$ + 10 ml dioxan, diluted 1 : 9 in $CDCl_3$	216	368
(VII)	0·015 ml $H_2{}^{16}O$ + 20 ml dioxan, diluted 1 : 4 in $CDCl_3$	234	370

[a] The experimental error in the determination of the shifts is estimated at ±1 Hz.

The 234—244 Hz signal observed for the $H_2{}^{16}O$ solutions must thus be due to their OH protons. The fact that an 0·1 ml + 10 ml dioxan solution exhibits this signal at 244 Hz while 0·02 ml + 10 ml dioxan and more dilute solutions display it at 234 Hz is the result of some self association still existing in the first solution and increasing the mean chemical shift of its OH protons. The OH shift observed for very dilute (water mole fraction *ca.* 10^{-3}) CCl_4–dioxan solutions of $H_2{}^{16}O$ was also found to be about 85 Hz smaller than their dioxan shift, at 56·4 MHz, which means an OH value of 2·06 p.p.m., as compared with the 2·34 p.p.m. shift obtained from our 234 Hz value at 100 MHz.[2]

Comparing the signals obtained for the ^{18}OH protons with those observed in the case of the ^{16}OH groups shows immediately (see Table) that the isotopic exchange of ^{16}O for ^{18}O lowers their chemical shift by 12—33 Hz (0·12—0·33 p.p.m.). The full extent of this unexpected decrease in the chemical shift of a proton covalently bonded to an ^{18}O atom, relative to the shift in the respective ^{16}O case, is exhibited for the 0·1 ml $H_2{}^{18}O$ + 10 ml dioxan (II) solution. In the case of the (IV) 0·02 ml $H_2{}^{18}O$ + 10 ml dioxan solution, part of the $H_2{}^{18}O$ present originally in the solution appears to have been exchanged with the water vapour content of the atmosphere by the time its n.m.r. spectrum has been measured, since although its OH signal appears 12 Hz higher than that of the corresponding $H_2{}^{16}O$ solution it is still much lower than the OH signals of the other $H_2{}^{18}O$ solutions investigated so far.

The OH shifts of the (V) and (VI) solutions, amounting to 208 and 216 Hz, respectively, must be the mean values for the ^{16}OH, the ^{17}OH, and the ^{18}OH groups, all present extensively in these solutions.

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[2] N. Muller and P. Simon, *J. Phys. Chem.*, 1967, **71**, 568.