Oxygen-17 Nuclear Magnetic Resonance Spectroscopy: Spin Coupling to Phosphorus-31

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Summary The one-bond reduced nuclear spin coupling $^1K(PO)$ is shown by $^1H-\{^{17}O\}$ INDOR experiments to be negative in $(MeO)_3P$ and in $(MeO)_2PHO$.

ALTHOUGH there have been a number of theoretical treatments[1,2] of nuclear spin–spin coupling constants involving oxygen, the low natural abundance (0·037%) and quad-

TABLE 1. Oxygen-17 n.m.r. parameters for organophosphorus species.

	Species	$^1J(^{31}P-^{17}O)/Hz$	$^1K(PO)/nm^{-3}$	$\Xi(^{17}O)/Hz^{a}$
(I)	$(MeO)_3P$	$+153 \pm 7$	$-23{\cdot}2 \pm 1$	$13{,}550{,}945 \pm 8$
(II)	$(MeO)_2PHO$	$+88 \pm 10$	$-13{\cdot}3 \pm 1{\cdot}5$	$13{,}556{,}704 \pm 12$
(III)	$(MeO)_2PHO$	$+220 \pm 10$	$-33{\cdot}5 \pm 1{\cdot}5$	$13{,}557{,}601 \pm 12$

[a] $\Xi(X)$ is the resonance frequency of X in a polarizing magnetic field of strength such that Me_4Si gives a proton resonance at 100 MHz.

rupole moment of ^{17}O, the only isotope with a nuclear spin ($I = 5/2, \mu < 0$), have previously permitted only one sign determination, that of $^1K(OH)$ in methanol.[3] This is particularly unfortunate, because it is in the region of the fifth and sixth groups of the periodic table that interesting changes of sign occur, and because it is necessary to know the signs of coupling constants in order to assess trends in their magnitudes. We therefore report here $^1H-\{^{17}O\}$ heteronuclear INDOR experiments which give the signs and magnitudes of $^1K(PO)$ for the formal linkages $P^{III}-O$, $P^{V}-O$, and $P^{V}=O$. These are of additional interest because many one-bond couplings to phosphorus are very sensitive to the oxidation state and hybridization of the phosphorus atom.

TABLE 2. Pattern of signs of reduced nuclear spin coupling constants between phosphorus and first row elements.

	B	C	N	O	F
3-Co-ordinate P	+ ve[a]	− ve[c]	− ve[d]	− ve[e]	− ve[f]
4 or 5-Co-ordinate P	+ ve[b]	+ ve[c]	± ve[d]	− ve[e]	− ve[f]

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The reaction sequence (1) was used to make trimethyl and dimethyl phosphite from methanol enriched to 10 atom % in ^{17}O, passage of gaseous nitrogen being used to

$$3MeOH + (Me_2N)_3P \rightarrow 3Me_2NH\uparrow + (MeO)_3P \xrightarrow{HCl} (MeO)_2PHO + MeCl\uparrow \qquad (1)$$

to remove final traces of the dimethylamine and methyl chloride also formed. In the absence of any isotope effect upon the course of the reactions the resulting proportions of singly substituted species should be: $(Me^{17}O)(MeO)_2P$ (I), 24·3; $(Me^{17}O)(MeO)PHO$ (II), 16·2; and $(MeO)_2PH^{17}O$ (III), 8·1%, with <3% of multiply substituted species which therefore may be ignored. ^1H N.m.r. spectra were recorded at 60 MHz, using *ca.* 30% solutions in methylene dichloride, and as in previous work[3] on methanol the rate of ^{17}O quadrupolar relaxation was found to be insufficient completely to average $^2J(^{17}O-H)$, thus making it possible to accumulate ^{17}O INDOR spectra at *ca.* 8·13 MHz by monitoring either component of the methoxy proton doublet. 64 scans sufficed to give ^{17}O signal-to-noise ratios in excess of 50:1 with recorded line widths of *ca.* 200 Hz, and from the spectra the magnitude of $^1J(^{31}P-^{17}O)$ was obtained together with its sign relative to that of positive $^3J(^{31}P-H)$ in species (I) and (II).[4] For species (III) $^4J(^{17}O-H)$ was too small to get ^{17}O INDOR spectra in this way, and it was necessary instead to monitor the weaker P–H resonances, 256 scans then being needed to give the magnitude of $^1J(^{31}P-^{17}O)$ and its sign relative to that of $^1J(^{31}P-H)$ which is known to be positive.[5]

The results are summarized in Table 1 and show that $^1K(PO)$ is negative for the three commonest types of phosphorus–oxygen linkage. This is in accord with theoretical predictions[1,2] and with the general trends for reduced coupling constants between phosphorus and other first-row nuclei, the general pattern being as depicted in Table 2. The increasing tendency towards more negative values as one moves to the right in the periodic table can be attributed to reduced *s*-overlap for the P-element bond, which leads to a progressive breakdown of the mean excitation energy approximation which is often used in descriptions of the Fermi contact interaction.[2] For the formal phosphorus–oxygen single bond it is noteworthy that although an increase in co-ordination number of phosphorus is accompanied by a decrease in the magnitude of $^1K(PO)$, this actually corresponds to a change to a more positive value, which is entirely analogous to the behaviour found for the couplings between phosphorus and carbon and nitrogen and fluorine. By contrast, the coupling $^1K(PSe)$ [and to some extent $^1K(PP)$] becomes more negative[6,7] when the oxidation state of phosphorus increases, and this may indicate a significant difference in the nature of the bond to phosphorus for first row and heavier elements. The considerably greater magnitude of $^1K(PO)$ associated with the formal double bond is entirely analogous to the behaviour of $^1K(PSe)$ in similar circumstances[8] and can be attributed substantially to changes in the hybridization of oxygen or selenium respectively.

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