^{31}P–H Spin Coupling in Protonated Tervalent Organophosphorus Compounds

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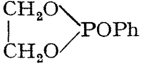
Summary $^1J(^{31}P–H)$ depends on the effective nuclear charge of phosphorus in addition to hybridization, in protonated tervalent phosphorus compounds.

IT is common practice[1] to use variations in nuclear spin–spin coupling constants to assess changes in the hybridization of the atoms involved. However, for directly bound atoms dominance by the Fermi contact interaction will also lead to a dependence of the coupling constant on the cube of the effective nuclear charge (Z_X) of either atom,[2] and the effect of this has been demonstrated[3] experimentally for $^1J(^{13}C–H)$. We now present evidence indicative of a similar *relationship* for $^1J(^{31}P–H)$ in a range of organophosphorus compounds.

N.m.r. parameters of tervalent phosphorus compounds in 100% *sulphuric acid*

	Substrate	$^1J(^{31}P–H)$ in Hz.	^{31}P Chemical shifts in p.p.m.[b] Substrate	Protonated species	Δ[c]
(1)	$(C_4H_9)_3P$	457±10	+ 32	−12	− 44
(2)	$(C_6H_{11})_2$	460±20	− 28	− 2	− 26
(3)	Me_2PhP	500±10	+ 46	+ 1	− 45
(4)	Ph_3P	506±2	+ 8	− 5	− 13
(5)	Ph_2POMe	553±2	−115	−56	+ 59
(6)	Ph_2PCl[a]	561±2	− 82	−46	+ 36
(7)	$PhPCl_2$[a]	653±2	−166	−41	+125
(8)	$(MeO)_2PhP$	666±2	−158	−54	+104
(9)	$(Pr^iO)_3P$	795±2	−138	−16	+122
(10)	$(EtO)_3P$	806±2	−139	−18	+121
(11)	 ..	822±2	−128	−16	+112
(12)	$(MeO)_3P$	830±2	−141	−26	+115
(13)	$(PhO)_3P$	870±2	−128	−10	+118

[a] HCl is evolved on dissolving in H_2SO_4 and the natures of the protonated species are not certain. We tentatively suggest $[Ph_2HPOSO_3H]^+$ and $[PhHP(OSO_3H)_2]^+$.
[b] Relative to 85% H_3PO_4. A positive sign indicates a high-field shift.
[c] Δ = Change in ^{31}P chemical shift on protonation.

When many organic derivatives of tervalent phosphorus are dissolved in 100% sulphuric acid, heat is evolved and the ^1H n.m.r. magnetic resonance spectrum of the fresh solution shows that a P–H bond has been formed, normally by direct protonation of the substrate to give a tetrahedral cation. ^{31}P–H coupling constants and ^{31}P chemical shifts are given in the Table. In several cases the resonances due to H directly bound to P were obscured by other lines in the proton spectrum, and $^1J(^{31}P–H)$ was then found by H–$\{^{31}P\}$ heteronuclear double resonance. This technique was also used to obtain the ^{31}P chemical shifts[4] and to confirm all assignments. Previously, direct ^{31}P n.m.r. has been used to study the protonation of organic phosphines, but the range of ^{31}P–H coupling constants observed was small.[5]

In order to account for the large range of $^1J(^{31}P–H)$ in these species solely in terms of phosphorus hybridization it would be necessary to postulate large variations in the inter-bond angles at phosphorus. This is unlikely in these tetrahedral species, and it appears that the major part of the variation arises from differences in the effective nuclear charge (Z_P) of phosphorus. Decrease of electron density at phosphorus will increase Z_P and hence $^1J(^{31}P–H)$ so the observed trend can be accounted for by the different inductive effects of the groups attached to phosphorus. Future attempts to use coupling to ^{31}P to assess phosphorus hybridization must take this into account.

With the exception of (6) and (7) [see footnote (a) to Table] there is an approximate monotonic correlation between $^1J(^{31}P–H)$ and Δ, the change in ^{31}P chemical shift occurring on protonation. Thus the latter can be related to the basicity of the substrate. There is a very good linear relation between $^1J(^{31}P–H)$ in the protonated species and the corresponding values of $^1J(^{183}W–^{31}P)$ recently reported[6] for the complexes $R_3PW(CO)_5$ (R = alkyl, alkoxy, *etc.*), and this indicates that the variations in the latter coupling constant are also dominated by changes in Z_P. Thus it appears that the observed correlation between $^1J(^{183}W–^{31}P)$ and the CO stretching frequency in the tungsten complexes can be interpretated by a mechanism involving σ-bonds only.[7]

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