The Nature of the Carbon–Phosphorus Bond in Methylidynephosphine

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Summary Nuclear magnetic resonance parameters have been determined for solutions of HCP, and a $^1J(^{13}CH)$ value of 211 Hz is rationalized in terms of *sp* hybridization at carbon, leading to a triple bond description of the CP bond; the appearance potential of the HCP^+ or DCP^+ ions from the parent molecules ($11{\cdot}4 \pm 0{\cdot}3$ eV) is close to a theoretical value.

The molecule HCP (methylidynephosphine) contains one of the few known examples of an isolated, unconjugated, multiple bond between carbon and phosphorus.[1] The nature of the CP bond in HCP has been inferred from i.r. studies including observations of a presumed CP stretching frequency[1] which have been subject to later questioning.[2] A microwave spectral study of HCP and DCP established the molecular geometry of the compound in the gas phase;[3] the CP bond length is compatible with triple bonding between carbon and phosphorus. In view of the considerable current interest in multiple bonding between carbon and third-row elements like silicon[4] and phosphorus,[5] we considered that a more detailed experimental investigation of bond character in HCP was desirable. We have therefore carried out an n.m.r. study of HCP in solution.

The samples of HCP were prepared by a simplified preparation, involving passage of phosphine (2—3 Torr) through a carbon arc.[1] Spectral studies of the volatile reaction products showed the presence of only three compounds: HCP, $HC{\equiv}CH$, and PH_3. Since the $HC{\equiv}CH$ and PH_3 did not interfere with the n.m.r. studies, (and, indeed, provided convenient internal references), all n.m.r. studies were carried out on this mixture either neat, or diluted with vinyl chloride, which was inert at the temperatures used (160—170 K). Above this temperature HCP rapidly polymerizes in solution. HCP signals were assigned on the basis of observed signal multiplicity, known spectra of all other components of the mixture, and the irreversible disappearance of the signals attributed to HCP when the spectral samples were allowed to warm to 200 K.

The spectral parameters were determined by Fourier transform techniques on a Bruker HFX-90 spectrometer and are as follows: $\delta(^{31}P)$ 32·0 p.p.m. upfield from 85% H_3PO_4 (ext.); $^2J(HCP)$ 43·9 Hz; $\delta(^{13}C)$ 154 p.p.m. downfield from Me_4Si (ext.); $^1J(^{13}CP)$ 54·0 Hz; $^1J(^{13}CH)$ 211 Hz.

The most immediately striking of these parameters, in terms of bonding in HCP, is the one-bond ^{13}C–H coupling constant of 211 Hz. A simple interpretation of this value, using the well known relationship[6] between $^1J(^{13}CH)$ and %*s* character in the CH bond, gives about 43% *s* character in the bond. Since electropositive atoms or groups, like the phosphorus atom[3] in HCP, generally decrease the value of $^1J(^{13}CH)$ below that predicted by hybridization alone, it is likely that the actual hybridization at carbon in HCP is very close to *sp*.

The one- and two-bond carbon–phosphorus coupling constants are relatively large in HCP. One-bond CP couplings are normally[9] small in 3-co-ordinate phosphorus compounds but increase as the positive charge on phosphorus increases. The normal range[10] for $^2J(HCP)$ is between 0 and 25 Hz, with phosphorus in its more usual co-ordination states. The high value of both one- and two-bond couplings in HCP emphasizes the high degree of *s* character in both bonds transmitting the coupling.

In summary, the n.m.r. data show that the molecule has a triple bond between carbon and phosphorus, presumably involving $2p_\pi$–$3p_\pi$ overlap,[11] and that it is polarized with phosphorus relatively positive: $HC^{\delta-}{\equiv}P^{\delta+}$; this is in accord with the moderate dipole moment[3] of HCP, with the known reaction[1] between HCP and HCl forming $MePCl_2$, and with detailed MO calculations on HCP.[11,12]

We have also determined, by direct electron impact studies,[13] the appearance potentials of the ions HCP^+

(11·4 ± 0·3 eV) and CP^+ (17·3 ± 0·5 eV) from HCP, and the ion DCP^+ (11·4 ± 0·3 eV) from DCP. The observed appearance potential of HCP^+ is somewhat larger than the ionization energy calculated for HCP by an *ab initio* MO method (9·5 eV),[11] but is quite close to one recently calculated using the MINDO/3 method[12] (10·7 eV).

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