

Isotope Effects in ^{31}P NMR of Phosphine

While isotope effects on NMR chemical shielding have been widely observed and neatly compiled, available data on isotope effects on NMR coupling constants are very limited (*1*). This is primarily due to their very small magnitudes. In this communication we report primary and secondary isotope effects observed in ^{31}P NMR of phosphine, which are somewhat larger than usual and in the opposite direction for coupling constants compared to those previously observed.

FT ^{31}P spectra of liquid and gaseous mixtures of PH_3 and PD_3 were observed. In the liquid at 227.0 K the lines are sufficiently narrow that precise measurements of coupling constants are possible. The spectra consisted of the expected number of multiplets which partly overlapped owing to the accidental near equality of the magnitudes of the P-D coupling constants and the chemical shifts upon isotopic substitution. Both were about 30 Hz. Assignment of the observed peaks was trivial and was confirmed with ^1H broadband decoupling. The results shown in Table 1 are statistical averages over spectra of several samples of the liquid mixtures at 227.0 K. The isotope effects do not appear to have any density dependence.

TABLE I
ISOTOPE EFFECTS ON THE COUPLING CONSTANTS AND
 ^{31}P CHEMICAL SHIELDING IN $\text{PH}_n\text{D}_{3-n}$ ^a

	$10^{-20} K_{\text{PH}}$ (cm^{-3})	$10^{-20} K_{\text{PD}}$ (cm^{-3})
PH_3	38.13	
PH_2D	37.88	40.63
PHD_2	37.62	40.22
PD_3		39.87
	^{31}P Chemical shift	
	$\Delta\nu$ (Hz)	$\Delta\sigma$ (ppm)
PH_3 - PH_2D	29.30	-0.804
PH_2D - PHD_2	30.76	-0.845
PHD_2 - PD_3	32.35	-0.888

^a The sign of the P-H coupling constant has been determined to be positive from ^1H NMR of partially oriented PH_3 in a nematic solvent (Ref. (*13*)).

The isotope effects on the ^{31}P chemical shielding in $\text{PH}_n\text{D}_{3-n}$ are similar to those observed for $\text{NH}_n\text{D}_{3-n}$ (*2*). The PH_3 - PD_3 ^{31}P isotopic chemical shift is rather large, 92.4 Hz at 36.42 MHz, i.e., $\sigma_{\text{PH}_3} - \sigma_{\text{PD}_3}$ is -2.54 ppm, whereas the NH_3 - ND_3 ^{15}N isotopic chemical shift is -1.96 ppm. As expected from observations by Batiz-Hernandez and Bernheim (*1*) in a large number of cases, the secondary isotope effect

on chemical shielding is found to be close to additive. However, a systematic deviation from true additivity is observed here. (See $\Delta\sigma$ values in Table 1.)

The reduced coupling constants, $K_{AB} = J_{AB}4\pi^2/h\gamma_A\gamma_B$, show both a primary and a secondary isotope effect. The magnitude of the primary isotope effect is 2.2 to $2.5 \times 10^{20} \text{ cm}^{-3}$, about 6% of the observed coupling constant, whereas the secondary isotope effect is 0.25 to $0.4 \times 10^{20} \text{ cm}^{-3}$ (0.7 to 1%) and is roughly additive. The isotope effects observed here are larger than any previously reported. In $^{15}\text{NH}_n\text{D}_{3-n}$ Litchman *et al.* (2) were unable to observe any isotope effects on the coupling constant.

The signs of the isotope effects observed here are unusual. The primary isotope effects on $^2K_{\text{HF}}$ ($\text{CHF}_3\text{-CDF}_3$) (3), on $^1K_{\text{PH}}$ in $(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{H}$ or D (4), and other four-coordinate phosphorus compounds (5), as well as the secondary isotope effects on $^1K_{\text{CH}}$ in some ^{13}C compounds (6, 7), on $^2K_{\text{HD}}$ ($\text{SiH}_3\text{D-SiHD}_3$) (8) and on $^1K_{\text{PH}}$ in four-coordinate phosphorus compounds (5) are all found to be negative. That is, $|K_{\text{heavy}}| < |K_{\text{light}}|$. Some of the above coupling constants are known to have positive signs, others negative signs. The signs of the isotope effects we observed in the coupling constants of $\text{PH}_n\text{D}_{3-n}$ are different from those observed previously. There has been a previous report of isotope effects of opposite signs in solutions of three- and four-coordinate ^{31}P in CD_3OD (5). However, since there are isotope effects due to differing hydrogen bonding abilities of H and D, as well as differing solvent effects on three- and four-coordinate phosphorus, a proper study of solvent effects is needed before these can be evaluated (4).

A simple qualitative interpretation of the isotope effects on coupling constants may be given as follows. The average bond extensions $\langle\Delta r\rangle$, $\langle(\Delta r)^2\rangle$, ... are generally known to be larger for lighter isotopes. In particular, microwave spectroscopy results indicate an average r of 1.4177 Å in PH_2D and 1.4116 Å in PHD_2 (9). The bond angle deformation is positive and is also larger for the lighter molecule. In PH_2D and PHD_2 the same microwave studies give an average α of $93^\circ 21.6'$ and $93^\circ 15.4'$, respectively (9). The average values of Δr and $\Delta\alpha$ appear in the Taylor series expansion commonly used in the interpretation of isotope effects (10):

$$K_{AB} = K_{AB}^{\text{eq}} + \left(\frac{\partial K_{AB}}{\partial \Delta r}\right)_{\text{eq}} \langle\Delta r\rangle + \left(\frac{\partial K_{AB}}{\partial \Delta\alpha}\right)_{\text{eq}} \langle\Delta\alpha\rangle + \left(\frac{\partial^2 K_{AB}}{\partial \Delta r^2}\right)_{\text{eq}} \langle(\Delta r)^2\rangle + \dots \quad [1]$$

From the limited information available, such as the variation of K_{HD} with internuclear distance in the HD molecule, the derivative $(\partial K_{AB}/\partial \Delta r)_{\text{eq}}$ might be expected to be positive for atoms A and B bonded to each other (11). This together with the larger average bond extension for lighter isotopes would lead to the usually observed change of K with isotopic substitution: $K_{\text{heavy}} < K_{\text{light}}$. The opposite effect in the phosphines may be due to (a) negative $(\partial K_{\text{PH}}/\partial \Delta r)_{\text{eq}}$, or (b) opposite sign of the $\Delta\alpha$ term, or (c) higher-order terms of opposite sign. The least likely possibility is (b) since there is some evidence to indicate that K_{AB} increases with increasing s character which accompanies an increase in bond angle in $\text{PH}_n\text{D}_{3-n}$, i.e., $(\partial K_{\text{PH}}/\partial \Delta\alpha)_{\text{eq}}$ positive (12). Data on the temperature dependence of the coupling constant in the isolated molecule would provide additional information since the dependence of K on temperature is also described by Eq. [1]. However, because of the greater linewidths observed in phosphine in the low-density gas, we were unable to obtain the temperature dependence for the isolated phosphine molecule.

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A. KEITH JAMESON

*Department of Chemistry
Loyola University
Chicago, Illinois 60626*

CYNTHIA J. JAMESON

*Department of Chemistry
University of Illinois at Chicago Circle
Chicago, Illinois 60680*

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