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THE BASICITY OF PHOSPHINAMIDES AND THE SITE OF PROTONATION[1]

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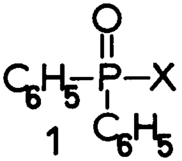
Phosphinamides (e.g., 1: X = NR_2) are strikingly labile in acidic solution.[2] A probable reason involves the N-protonated amide (2) as the reactive species.[2] We have been able to evaluate pK_{BH^+} values for phosphinamides, and we have some evidence concerning the dominant form of the conjugate acid (2 or 3).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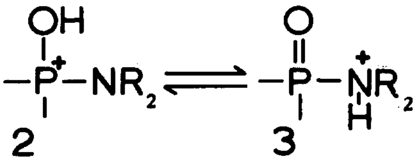
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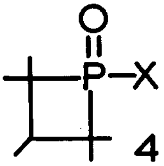
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Although 1 (X = NR_2) hydrolyzes very rapidly in acid,[2] 4 (X= NR_2) reacts slowly enough[3] so that it is possible to observe nmr spectra over a range of acid concentrations. Therefore, we **have measured** pK_{BH+} (pK_a of protonated 4) values by the method[4] which involves determination of chemical shifts as a function of acidity. The results are:

Compound	Solvent[a]	Observed Chem. Shifts	pK_{BH+}
4: X = $N(CH_3)_2$	Dioxane-H_2O(5:95)	$N(CH_3)_2$[b]	-1.7
4: X = $NHCH_3$	"	$N-CH_3$[c]	-3.2
4: X = OCH_3	H_2O	$O-CH_3$[c]	-5.2

[a] H_2SO_4 added:

[b] Relative to $(CH_3)_4N^+$ and $(CH_3)_3{}^+NOH$ - both gave pK_{BH+} = -1.7

[c] Relative to $(CH_3)_4N^+$

The large difference in pK' s of the mono and dimethylamides suggests N-protonation; such a large substituent effect would be unlikely if there were O-protonation (in carboxylic amides,[5] methyl substitution causes small effects).

Observation of J(P-X-C-H) in a series of phosphinate esters and phosphine oxides, protonated and unprotonated, reveals that in every case protonation results in an increase in coupling constant.[4] However, protonation of phosphinamides causes a decrease in J(P-N-C-H).[6] Representative data are:

Compound	**1**: X = OCH_3	$(CH_3CH_2)_3PO$	**1**: X = $N(CH_3)_2$	**4**: X = $N(CH_3)_2$	**4**: X = OCH_3
.J($CHCl_3$)(Hz)	11.1	16.6(D_2O)	11.1	10.2	10.0
J(H_2SO_4)(Hz)	12.1	19.5	10.0	7.9	10.7

These data also suggest N-protonation of the amides in contrast to the O-protonation which must be true for the esters and oxides. The increases in coupling are probably due to the increase in positive charge on phosphorus[7] resulting from O-protonation. The decrease in coupling on protonation of the amides is probably due to decrease in the P-N bond order and decrease in the s-character in the nitrogen sigma bonding orbitals resulting from N-protonation: both effects should cause a decrease in J(P-N-C-H). Further research will be required to determine if this technique is a reliable tool for detecting point of protonation.

This hypothesis of N-protonation of phosphinamides must be tested further and may not extend to all phosphorus amides. However, it is relevant that the nitrogen atom in **1** (X = $N(CH_3)_2$ is non planar; the CNC angle is 114°.[8] This is in marked contrast to the planar nitrogen in carboxylic amides which O-protonate.

REFERENCES

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