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## Proton Resonance Frequencies in Several Organophosphorus Acids<sup>1</sup>

K. DARRELL BERLIN and M. NAGABHUSHANAM

Department of Chemistry, Oklahoma State University, Stillwater

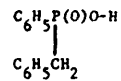
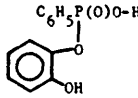
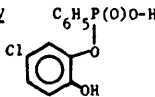
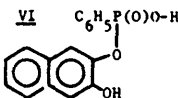
Increasing interest in organophosphorus compounds has stimulated efforts to elucidate their structures by nuclear magnetic resonance (N.M.R.) (Berlin and Nagabhushanam, 1964; Ferraro and Peppard, 1963; Hendrickson *et al.*, 1964; Siddall and Prohaska, 1962). In the present work, several new phosphorus acids have been examined and several useful solvent systems have been uncovered. In addition, acids of the type  $R_2P(O)OH$  were examined, which had not been studied previously (Ferraro and Peppard, 1963). In Table I it is clear that the protons of the compounds investigated display singlets at low field, which indicates rapid proton exchange.<sup>2</sup> Acetone proved to be the most useful solvent as the acids were very sparingly soluble in such common media as carbon tetrachloride, carbon disulfide, chloroform and benzene. In acetone, dimethyl sulfoxide (DMSO), and methylene chloride the range observed for the acidic protons was  $\delta$  10.28-11.90 measured from tetramethylsilane (TMS) as the internal standard. Acid III, examined neat (except for a drop of TMS), gave two broad peaks at  $\delta$  7.54 and  $\delta$  4.28, the former apparently

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<sup>2</sup>Models, such as hydroxyacetic and salicylic acids, also showed one peak for protons on oxygen in acetone solution.

Table I. NMR Data of Organophosphorus Acids.

CPD	$\delta$ - values (J=cps)			Solvent
	PO-H	Aromatic Protons	-CH <sub>2</sub> -	
<u>I</u> (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)O-H	11.52	7.67*		Acetone
	6.46	7.6*		TMU
<u>II</u> 	10.28	7.50*	3.24 (J=17)	DMSO
<u>III</u> (HOCH <sub>2</sub> ) <sub>2</sub> P(O)O-H	6.85		3.87 (J=5)	TMU
	7.54		4.28	None
<u>IV</u> 	10.84	7.40*		Acetone
<u>V</u> 	10.78	7.50*		Acetone
<u>VI</u> 	10.30	7.65*		Acetone
<u>VII</u> C <sub>6</sub> H <sub>5</sub> P(O)(O-H) <sub>2</sub>	11.52	7.67*		Acetone
	12.36 (satd.)	7.50*		TMU
<u>VIII</u> ClCH <sub>2</sub> P(O)(O-H) <sub>2</sub>	11.90		3.73 (J=11)	Acetone
			3.94 (J=11)	D <sub>2</sub> O
<u>IX</u> HOCH <sub>2</sub> P(O)(O-H) <sub>2</sub>	9.52		3.78 (J=7.5)	TMU

\*Multiplet center

the result of rapid proton exchange between the three hydroxyl groups; in tetramethylurea (TMU) both resonance peaks were shifted to higher field. TMU was also found to be the only useful solvent for **IX**. Splitting of the peak by phosphorus at higher field served to identify the methylene hydrogens ( $J_{P-H} = 5$  c.p.s.) in both solvents.

Apparently, the phosphoryl group de-shields the acidic proton; this is analogous to the effect observed with the acidic protons of carboxylic acids.

The effect of dilution<sup>1</sup> on the chemical shift for the acidic protons of **VII** was determined over a twenty-five fold concentration change in acetone. If  $\delta$  is plotted against concentration (Fig. 1), clearly a sharp change

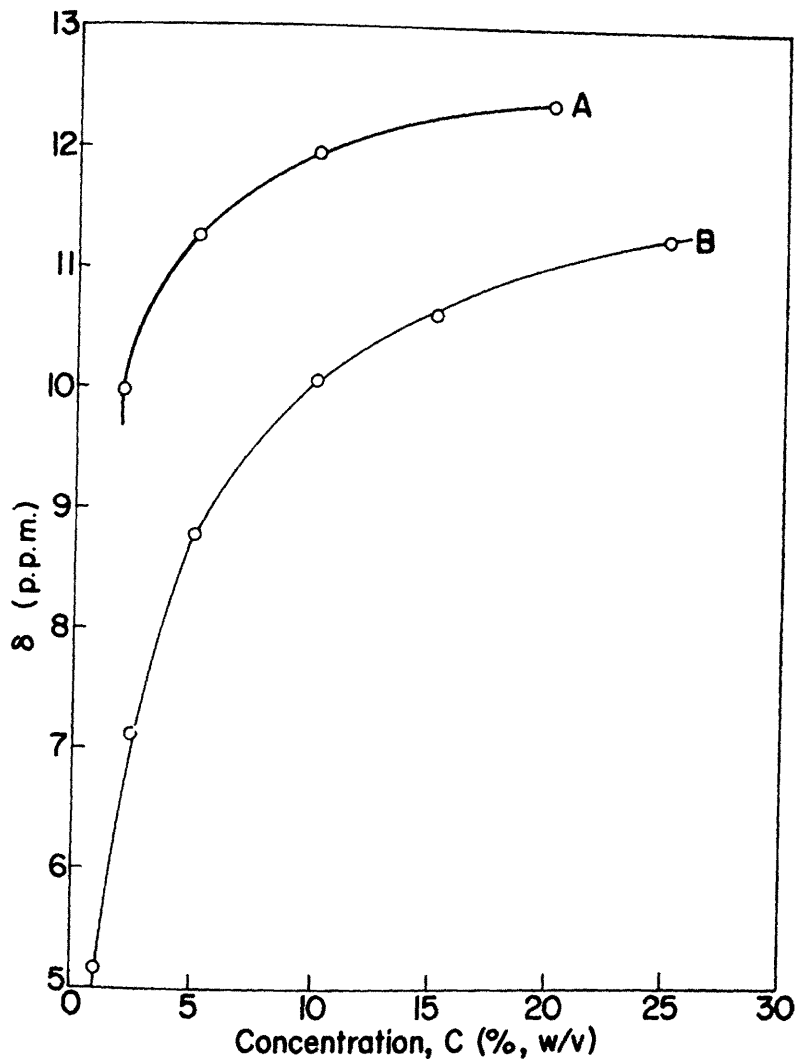


Fig. 1. Dilution curves of VII in TMU (A) and acetone (B).

a slope is observed below 10% with either acetone or TMU as solvent. This agrees well with data on phosphoric acids  $[\text{RO}]_2\text{P}(\text{O})\text{OH}$  and hydrogen phosphonates  $[(\text{RO})\text{R}'\text{P}(\text{O})\text{OH}]$  (Ferraro and Peppard, 1963). When the data were plotted on a log-log graph (Fig. 2), a straight line resulted for both solvents but the slopes differed. If intermolecular as-

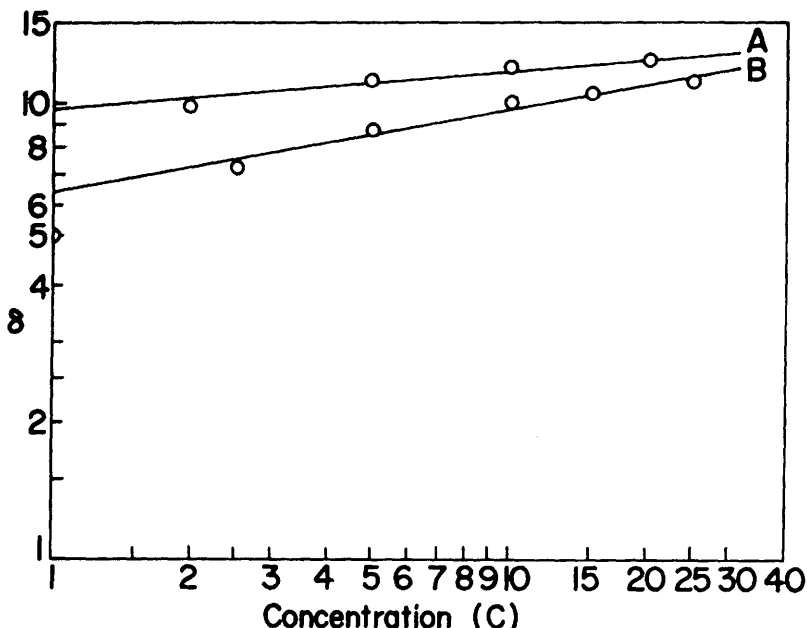


Fig. 2. Log-log plot of dilution line of VII in TMU (A) and acetone (B).

sociation<sup>4</sup> is operative in acetone and TMU, it appears the complex must dissociate at concentrations between 5 and 10 per cent. A possible formulation of the associated complex is one involving H-bonds that resembles this complex formed by carboxylic acids, except for the presence of the second hydroxyl group.

Since only one peak is visible for the acidic hydrogens, it is assumed that rapid exchange must occur between the hydrogens involved in the dimeric complex and those protons bound to solvent. The dilution curves are remarkably similar to that observed upon dilution of acetic acid in acetone.<sup>1</sup>

A chain-like polymer involving H-bonded, symmetrical units of VII cannot be eliminated from consideration. However, existence of an extended polymer seems less likely since preservation of a structure of this type in a polar medium capable of H-bonding would require that the H-bonds be unusually strong. A close analogy is the observation that in a number of polar solvents, such as acetone, acetic acid, ethanol, and ether, benzoic acid exists only in the monomeric form (Pauling, 1960).

Courtauld models indicate that in the tetragonal phosphorus atom it is difficult to align orbitals on the phosphoryl oxygen atom and on the proton to form a H-bonded dimeric complex from two molecules; certainly,

<sup>1</sup>It has been noted that acetone caused pronounced dilution effects on the chemical shifts of acidic protons in acetic acid (C. M. Huggins, et al., 1956).

<sup>4</sup>This is similar to molecular association (or a type of dimerization) believed to occur with carboxylic acids (C. M. Huggins, et al., 1956).

a planar structure cannot be obtained. This might be a partial explanation for the dissociation of the complex from VII at high concentration in acetone or TMU. The difference in slopes in Fig. 2 is understandable, as these solvents would not have the same ability to form H-bonds with the solute.

## EXPERIMENTAL

Acids I, II, III, VII, and VIII were commercially available while acids IV-VI were prepared by a known method reported from this laboratory (Berlin and Nagabhushanam, 1964). Except in the dilutions studies shown in Fig. 1, the N.M.R. spectra were obtained on saturated solutions of the acids at room temperature using a Varian A-60 spectrometer and TMS as an internal standard.

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