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Phosphorus-31 NMR Data for Some Miscellaneous Compounds

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Phosphorus-31 chemical shifts are reported for 61 organophosphorus compounds, which include six secondary phosphines, seven chlorophosphines, 28 tertiary phosphines, eight quaternary phosphonium salts, seven ylides, and several miscellaneous compounds. The preparation of iodomethyltriphenylphosphonium methyl sulfate and iodomethyltriphenylphosphonium hexafluorophosphate is reported.

Over the past several years we have collected phosphorus NMR data on some miscellaneous compounds which we have not previously reported (Table I). Some experimental results are given for several compounds which will not be reported elsewhere.

An interesting case of metathesis occurred during an attempt to obtain soluble phosphonium salts from a slightly soluble phosphonium iodide.

Iodomethyltriphenylphosphonium iodide (*9*), which is prepared by the reaction of triphenylphosphine and methylene iodide, is not soluble enough to permit measurement of the ^{31}P chemical shift under our conditions. One usual procedure for conversion of iodide salts to compounds of other anions—viz., treatment of the phosphonium salt with freshly prepared silver oxide, filtration, and addition of the acid of the desired anion—failed in this case because of apparent side reactions of the iodomethyl groups. Several other attempts to form a soluble salt by metathesis also failed. However, treatment of iodomethyltriphenylphosphonium iodide with freshly distilled dimethyl sulfate produced the soluble methyl sulfate salt:

$$[(C_6H_5)_3PCH_2I]I + (CH_3O)_2SO_2 \rightarrow [(C_6H_5)_3PCH_2I][CH_3OSO_3] + CH_3I$$

EXPERIMENTAL

Phosphorus-31 NMR measurements were obtained as described elsewhere (*4*) on a Varian DP60 NMR spectrometer. The chemical shifts are reported for 85% H_3PO_4 as the standard. The measurements were made at 22° ± 2° C.

Proton measurements were obtained on a Varian A60A spectrometer.

Iodomethyltriphenylphosphonium Methyl Sulfate. Iodomethyltriphenylphosphonium iodide (5.0 grams, 9.4 mmoles) was placed in a flask under N_2. Methylene chloride (35 ml) was added and the mixture was stirred overnight at room temperature. Most of the solvent was removed under vacuum and addition of ether caused precipitation of the product, which was recrystallized from isopropyl alcohol after treatment with decolorizing carbon. The yield was 3.3 grams (86%) of light yellow crystals (m.p. 179–81°). The proton NMR gave three peaks: a multiplet at 2.08 τ, a doublet at 4.89 τ ($^2J_{PCH}$ = 7.8 Hz), and a singlet at 6.35 τ, of intensities 15.3:2.0:2.9, respectively. The peaks are due to the phenyl, methylene, and methyl groups with the expected ratio of 15:2:3.

Anal. Calcd. for $C_{20}H_{20}IO_4PS$: C, 46.75; H, 3.89. Found: C, 46.88; H, 4.15.

Iodomethyltriphenylphosphonium Hexafluorophosphate. This compound was made from the methyl sulfate salt

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Table I. Phosphorus Chemical Shifts of Some Organophosphorus Compounds

Compound	Chemical Shift, PPM	Solvent	Other
Secondary phosphines			
$(\mathit{tert}\text{-}C_4H_9)_2PH$	−20.1	Neat	$J_{PH} = 197$
$(\mathit{tert}\text{-}C_4H_9)(C_6H_5)PH$	−5.7	Neat	$J_{PH} = 200$
$(\mathit{p}\text{-}CH_3C_6H_4)_2PH$	42.9	Neat	$J_{PH} = 212$
$(\mathit{m}\text{-}CH_3C_6H_4)_2PH$	40.2	Neat	$J_{PH} = 214$
$(\mathit{o}\text{-}CH_3C_6H_4)_2PH$	59.1	Neat	$J_{PH} = 219$
$(\mathit{p}\text{-}(CH_3)_3CC_6H_4)_2PH$	43.9	Neat	$J_{PH} = 212$
Halophosphines			
$(\mathit{tert}\text{-}C_4H_9)(\text{iso-}C_3H_7)PCl$	−138.9	Neat	
$(CH_2{=}CHCH_2)(C_6H_5)PCl$	−86.0	Neat	
$(C_6H_5CH_2)(C_6H_5)PCl$	−86.5	Neat	
$(\mathit{tert}\text{-}C_4H_9)_2PCl$	−144	Neat	
$(\mathit{tert}\text{-}C_4H_9)(C_6H_5)PCl$	−69.6	Neat	
$(\text{iso-}C_3H_7)PCl_2$	−198.6	Neat	
$(\mathit{tert}\text{-}C_4H_9)PCl_2$	−197.5	Neat	
Tertiary phosphines			
$(\mathit{n}\text{-}C_4H_9)_2(\mathit{tert}\text{-}C_4H_9)P$	4.6	Neat	
$(\mathit{n}\text{-}C_4H_9)(\mathit{tert}\text{-}C_4H_9)_2P$	−26.6	Neat	
$(\mathit{sec}\text{-}C_4H_9)_3P$	−8.0	Neat	−7.8[a]
$[(C_2H_5)_2CH_3C](C_6H_5)_2P$	−11.4	Neat	
$(CH_2{=}CHCH_2)(\mathit{tert}\text{-}C_4H_9)(\mathit{iso}\text{-}C_3H_7)P$	−14.4	Neat	
$(CH_2{=}CHCH_2)(C_6H_5CH_2)(C_6H_5)P$	20.7	Neat	
$(CH_2{=}CHCH_2)_2(C_6H_5)P$	27.5	Neat	
$(CH_2{=}CHCH_2)_2(\mathit{tert}\text{-}C_4H_9)P$	6.0	Neat	
$(CH_2{=}CHCH_2)(CH_3)(\mathit{tert}\text{-}C_4H_9)P$	18.2	Neat	
$(\mathit{p}\text{-}CH_3C_6H_4)_3P$	8.0	CH_2Cl_2	
$(\mathit{p}\text{-}CH_3OC_6H_4)_3P$	10.2	CH_2Cl_2	
$(\mathit{p}\text{-}ClC_6H_4)_3P$	8.5	CH_2Cl_2	9.2[b]
$(\mathit{p}\text{-}CF_3C_6H_4)_3P$	6.0	CH_2Cl_2	
$(\mathit{p}\text{-}(CH_3)_2NC_6H_4)_3P$	11.5	CH_2Cl_2	
$(\mathit{p}\text{-}(CH_3)_3CC_6H_4)_3P$	9.1	CH_2Cl_2	
$(\mathit{p}\text{-}FC_6H_4)_3P$	9.0	CH_2Cl_2	8.8[c]
$(\mathit{p}\text{-}CH_3SC_6H_4)_3P$	8.3	CH_2Cl_2	
$(\mathit{p}\text{-}BrC_6H_4)_3P$	8.2	CH_2Cl_2	
$(\mathit{p}\text{-}(CH_3)_2CHC_6H_4)_3P$	7.8	CH_2Cl_2	
$(\mathit{p}\text{-}(CH_3)_3SiC_6H_4)_3P$	5.8	CH_2Cl_2	
$(\mathit{m}\text{-}CH_3C_6H_4)_3P$	5.3	CH_2Cl_2	
$(\mathit{m}\text{-}CH_3OC_6H_4)_3P$	2.1	CH_2Cl_2	
$(\mathit{m}\text{-}ClC_6H_4)_3P$	4.4	CH_2Cl_2	
$(\mathit{m}\text{-}CF_3C_6H_4)_3P$	5.0	CH_2Cl_2	
$(\mathit{m}\text{-}(CH_3)_3SiC_6H_4)_3P$	5.6	CH_2Cl_2	
$(\mathit{o}\text{-}CH_3C_6H_4)_3P$	30.0	CH_2Cl_2	
$(\mathit{o}\text{-}CH_3OC_6H_4)_3P$	38.5	CH_2Cl_2	
$(\mathit{o}\text{-}CF_3C_6H_4)_3P$	18.5	CH_2Cl_2	
Quaternary phosphonium Salts			
$[(CH_2{=}CHCH_2)(C_6H_5CH_2)_2(C_6H_5)P]Br$	−24.3	CH_3OH	
$[(CH_2{=}CHCH_2)_2(C_6H_5CH_2)(C_6H_5)P]Br$	−24.2	CH_3OH	
$[(CH_2{=}CHCH_2)_2(\mathit{iso}\text{-}C_3H_7)(\mathit{tert}\text{-}C_4H_9)P]PF_6$	−40.8	DMSO	
$[(CH_2{=}CHCH_2)_2(CH_3)(\mathit{tert}\text{-}C_4H_9)P]Br$	−38.7	CH_3OH	
$\{(CH_2{=}CHCH_2)_2[(C_6H_5)_2CH](C_6H_5)P\}Br$	−24.0	CH_3OH	
$[(CH_2{=}CHCH_2)(C_6H_5CH_2)(CH_3)(C_6H_5)P]Br$	−25.5	CH_3OH	
$[(CH_2{=}CHCH_2)(\mathit{iso}\text{-}C_3H_7)(CH_3)(\mathit{tert}\text{-}C_4H_7)P]PF_6$	−44.1	DMSO	
$[(C_6H_5)_3(CH_2I)P]CH_3OSO_3$	−24.3	DMSO	
Phosphorus ylides			
$(C_6H_5)_3P{=}CHCl$	−25.1	DMSO	
$(C_6H_5)_3P{=}CHI$	−19.7	DMSO	
$(C_6H_5)_3P{=}CH(C_6H_5)$	−7.1	DMSO	
$(CH_3)(C_6H_5)_2P{=}CH_2$	−11.4	DMSO	
$(CH_3)_2(C_6H_5)P{=}CH_2$	−6.4	DMSO	
$(C_6H_5)_3P{=}CHCOOCH_3$	−17.3	DMSO	−17.6[d]
$(C_6H_5)_3P{=}CHCOCH_3$	−14.5	CH_2Cl_2	
Other compounds			
$(C_6H_5)_3P{=}Se$	−35.2	CH_2Cl_2	−35.0[e]
$(CH_3)(C_6H_5)_2P{=}Se$	−22.9	CH_2Cl_2	
$(C_2H_5)_2NP(C_4H_9)_2$	−53.5	CH_2Cl_2	
$[\mathit{p}\text{-}(CH_3)_3CC_6H_4]_3P{=}O$	−31.4	CH_2Cl_2	
$[\mathit{p}\text{-}(CH_3)_2SiC_6H_4]_3P{=}O$	−30.0	CH_2Cl_2	

[a] *(3)*. [b] *(6)*. [c] *(2)*. [d] *(7)*. [e] *(8)*.

and ammonium hexafluorophosphate by metathesis in aqueous solution. After recrystallization from acetone by the slow addition of water, the product melted at 248-51°.

Anal. Calcd. for $C_{19}H_{17}F_6IP_2$: I, 23.20. Found: I, 23.49.

Ylides. The air-sensitive ylides were prepared by reaction of the quaternary phosphonium salt with a freshly prepared solution of dimethylsulfinyl carbanion in DMSO (*1*, *5*).

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Partial Molal Volumes of *p*-Toluenesulfonic Acid, Sodium *p*-Toluenesulfonate, Iodic Acid, and Sodium Iodate in Aqueous Solutions at 25°C

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Partial molal volume data are reported for *p*-toluenesulfonic and iodic acid and their sodium salts. *p*-Toluenesulfonic acid exhibits strong acid behavior similar to that of hydrochloric acid, in that the partial molar volume of the sodium salt at infinite dilution is smaller than that of the acid. The behavior of iodic acid in very dilute solutions resembles somewhat that of acetic acid.

Ionization constants as calculated from Raman spectral data have been reported in recent years for both iodic acid (*1*) and *p*-toluenesulfonic acid (*2*). The molar volume of a weak electrolyte decreases upon ionization (*5*), and therefore it seemed desirable to investigate the behavior of these two acids which have ionization constants intermediate between those of a weak acid such as acetic and strong acids such as hydrochloric acid.

EXPERIMENTAL

Solutions of iodic acid, sodium iodate, and sodium *p*-toluenesulfonate were prepared by adding weighed amounts of the solids to known weights of triple-distilled water. Iodic acid and sodium iodate were reagent grade, used as received. The reagent-grade sodium *p*-toluenesulfonate was twice recrystallized from cold water and showed no trace of sulfate or chloride impurities. It was necessary to correct the iodic acid concentrations to account for the small amount of I_2O_5 which is present in dry HIO_3. This fraction was determined from the experimental equivalent weight found for HIO_3. *p*-Toluenesulfonic acid solutions were prepared by gravimetric dilution of a concentrated stock solution of the acid.

The volume of the Sprengel-Ostwald pycnometer was determined from its weight when filled with water. The capillary volumes were determined with mercury, using the handbook value for the density of mercury. After the filled pycnometer was weighed each time, it was placed in a water bath controlled to 25.00° ± 0.01° and the volume of the liquid was calculated from its level in the capillary arms. Density values for 0.5 and 1.0*m* NaCl, which were used as a check on the pycnometer calibration, varied from those in the literature by a maximum of 5 units in the last significant figure.

Apparent molal volumes were first calculated at the measured concentrations from the equation

$$\phi_v = 1000(\sigma_0 - \sigma)/mo\sigma_0 + M_2/\sigma$$

These data were plotted and partial molal volumes were calculated from the smoothed data by the equation

$$\overline{v}_2 = \phi_v + m^{1/2}/2\ d\phi/dm^{1/2}$$

The apparent molal volume calculated from the new data differed from the smoothed values by a maximum of 0.5% in one instance and by an average of 0.15%.

RESULTS AND DISCUSSION

Raw density data are presented in Table I and partial molal volume data at rounded concentrations, as calculated from the smoothed data, are given in Table II. Iodic acid with an ionization constant of 0.17 (*1*) and toluenesulfonic acid with an ionization constant of 11.6 (*2*) represent electro-