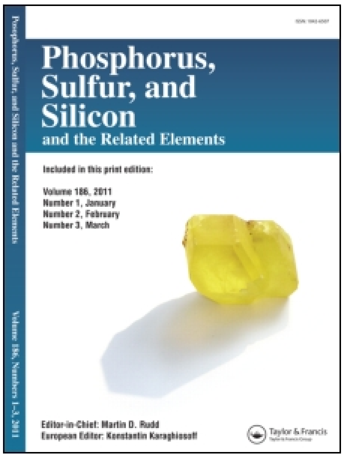

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A ^{31}P NMR STUDY OF THE WATER SOLUBLE DERIVATIVES OF 1,3,5-TRIAZA-7-PHOSPHAADAMANTANE (PTA)

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1,3,5-Triaza-7-phosphaadamantane (PTA), a small air stable aliphatic phosphine, and some water soluble derivatives have been studied mainly using ^{31}P nmr. PTA has been shown to have a pKa of 6.0 but this basicity does not relate to the phosphorus atom but one of the nitrogen atoms in the molecule. Alkyl halides similarly add to one of the nitrogens and conductivity and nmr studies indicate that these are ammonium salts. Oxidation and the reaction with sulphur and selenium occur at phosphorus, indicated by large ^{31}P coordination chemical shifts. All the derivatives prepared are water soluble.

Key words: ^{31}P nmr; 1,3,5-Triaza-7-phosphaadamantane; water soluble phosphine; coordination chemical shifts.

PTA, first prepared in 1974,[1] has only received limited attention.[2–4] Darensbourg's study of a few metal carbonyl complexes[3] and the determination of the crystal structure of $(CO)_5MoPTA$[4] appear to be the only study of metal complexes of this potentially important ligand. The small cone angle (102°), air stability, water solubility and potentially quadridentate non-chelating nature of PTA make this an unusual phosphine ligand. Darensbourg indicated that the similarity of force constants of $\nu(CO)$ and the ^{31}P coordinate chemical shifts in the complexes $(CO)_5MoL$ ($L = PMe_3$, or PTA) would make the easily handled PTA a suitable alternative to PMe_3 as a ligand for transition metals.

A further potential of PTA lies in its ability to form water soluble organic derivatives. Thus, we decided to investigate the properties of PTA and its organic derivatives as a prelude to investigating its metal complexes. This preliminary report using principally multinuclear nmr techniques is designed to indicate some of the properties of PTA and its derivatives.

The ^{31}P chemical shifts of PTA in various solvents ranges from $\delta = -104.4$ in the solid state to -96.2 in aqueous solution. This is rather a large range for a phosphine but it may reflect a strong solvent interaction at the nitrogen atoms e.g. hydrogen bonding in the case of water.

The pKa determined by simple aqueous acid-base titration gave a value of 6.0. Only one equivalence point was detected indicating only monoprotonation in the presence of 0.1 M acid. The protonated species showed no phosphorus-proton coupling, expected to have a magnitude of *ca.* 500 Hz,[5] though rapid exchange in aqueous solution may negate its observation. However, one *in situ* sample of

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TABLE I

^{31}P nmr data of PTA and derivatives in aqueous solution

Compound	$\delta^{31}P$	Δ*
PTA	−96.2	—
$PTAMe^+I^-$	−85.0	11.2
$PTAEt^+I^-$	−84.4	11.8
$PTACH_2C_6H_5^+Cl^-$	−82.2	14.0
PTA oxide	−2.0	94.2
PTA sulphide	−17.4	78.8
PTA selenide†	−31.4	64.8
PTAMeI selenide‡	−21.2	75.0
$PTAH^+Cl^-$ §	−89.9	6.3

* Δ is the coordination chemical shift = $\delta_{complex} - \delta_{free\ ligand}$, Δ is calculated from PTA in aqueous solution.

† $J(^{31}P-^{77}Se) = 760$ Hz (MeOH solution 219°K)

‡ $J(^{31}P-^{77}Se) = 794$ Hz (MeOH solution room temperature)

§ Only this sample gave a well resolved undecoupled spectrum showing $^3J(^1H-^{31}P) = 9.2$ Hz

PTA in aqueous HCl solution gave a ^{31}P nmr spectrum composed of a doublet at −89.9 ppm which we attribute to three-bond coupling with $^3J(^1H—^{31}P) = 9.2$ Hz. A sample of PTA (0.2 M) and CF_3CO_2H(0.2 M) in CH_3OD (measured at 193 K to minimize proton exchange) gave a ^{31}P nmr peak at −90.1 ppm. The occurrence of these peaks for protonated species in the same region as found for *N*-alkylated species (Table I) is thus consistent with protonation at N also. Similarly, our observation of a ^{31}P nmr peak at −88.8 ppm for a solution containing BF_3 and PTA in methanol would appear to indicate *N*-donor complexation for BF_3, as expected for a "hard" Lewis acid. The pKa of 6.0 for PTA is therefore best compared with the value of 6.2 for hexamethylenetetramine and not the values found for other phosphines such as those obtained by Allman[5] and Angelici[6] (e.g., $pK_a = 8.65$ for PMe_3). Whereas the proton interacts with one of the nitrogen atoms metal complexes can form metal-phorphorus bonds as shown by Darensbourg.[3] We have also prepared complexes such as $PTAHgX_2$, $(PTA)_2PtCl_2$ and $(PTA)_3RhCl_3$ in which coupling indicates metal to phosphorus binding.[7]

The reaction of PTA with excess alkyl halide produced only monoalkylated species (Table I). The ^{13}C nmr of the methylated species indicated that the methyl group was a singlet at δ 52.7 and that the methylene groups between

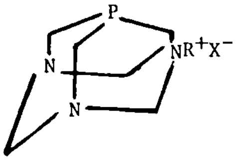
TABLE II

Conductivities of PTA derivatives, 1×10^{-3} M solutions at 25°C

Compound	$\Lambda_m(H_2O)$	$\Lambda_m(DMSO)$
PTAMeI	114	34.5
PTAEtI	115	38.5
$PTACH_2C_6H_5Cl$	127	42.8

nitrogen and phosphorus were inequivalent giving doublets at 48.0 and 59.2 in the ratio 2:1. Conductivity studies (Table II) of the PTA derivatives in aqueous solution and in DMSO gave values that indicate the derivatives are 1:1 electrolytes. Simple aqueous titrations indicated that the methyl iodide derivative of PTA could not be protonated in 0.1 M acid solution. Thus, neither the phosphorus atom nor the other two nitrogen atoms were basic to aqueous acid.

The above evidence leads us to agree with Daigle[1,2] that the alkyl halide derivatives are of the form:



Oxidation or the reactions of PTA with sulphur or selenium in aqueous solution produced the water soluble phosphine oxide, sulphide and selenide respectively. The large ^{31}P chemical shifts and the observation of selenium satellites in the low temperature methanol spectrum of the selenide attest to the bonding at the phosphorus atom. The large size of the coordination chemical shifts indicates a strong interaction between phosphorus and the Group VII atoms.

The observation of $^{1}J(^{31}P—^{77}Se)$ for PTA allows an assessment of the phosphorus basicity. The correlation between the coupling constant, which has a negative sign, and the electronegativity of the substituent is well documented.[8,9] For example, phosphites of low σ basicity due to the electronegative alkoxy groups have $^{1}J(^{31}P—^{77}Se)$ values in the 900–1100 Hz range. Strongly basic trialkyl phosphines have coupling constants near 700 Hz for their selenides. PTA selenide having a $J(^{31}P—^{77}Se)$ value of 760 Hz would appear to be a weaker σ donor than PEt_3 (705 Hz) and $P(C_6H_5)_3$ (735 Hz). However, the results we have obtained for mercury complexes of the form $PTAHgX_2$ tend to contradict this conclusion. The problem may arise in trying to compare ligands with very different cone angles i.e. PEt_3 (cone angle 132°) and PTA (cone angle 102°). A similar comparison has been made between $P(NMe_2)_3$ cone angle 157°, $J(^{31}P—^{77}Se) = 784$ Hz and $P(\overline{NCH_2CH_2})_3$ cone angle 108°, $J(^{31}P—^{77}Se) = 851$ Hz[8] where $P(\overline{NCH_2CH_2})_3$ is able to form $[AgL_4]X$ complexes indicating it is basic enough to exclude halides from the coordination shell.

The methyl iodide derivative of PTA forms a selenide with $J(^{31}P—^{77}Se) = 794$ Hz in methanol solution. Assuming no great change in cone angle for these two derivatives the coupling constant increase probably indicates a reduction of the basicity of the phosphorus in the alkyl halide derivative.

EXPERIMENTAL

^{31}P nmr spectra were recorded on Bruker WH-400 or Bruker AM-250 spectrometers using TMP as external standard.

Conductivity measurements of 1×10^{-3} M solutions at 25° were made using an AlM 6451 LCR Databridge.

Microanalyses were carried out by M-H-W Laboratories, Phoenix, AZ.

PTA was prepared by the method of Daigle and recrystallized from methanol. A ^{13}C nmr spectrum gave a doublet at δ 50.3 (J = 17.8 Hz) and a singlet at δ 73.4. The methyl iodide derivative of PTA, 1-methyl-1-azonia-3,5-diaza-7-phosphaadamantane iodide was prepared by the reaction of a slight molar excess of methyl iodide with PTA dissolved in methanol. The compound was recrystallized from methanol. ^{13}C nmr (D_2O) δ 48.0 (d) (J = 21.3 Hz), 52.7 (s), 59.2 (d), (J = 33.5 Hz), 71.8 (s), 82.7 (s). The ethyl iodide derivative of PTA was prepared by the reaction of a slight excess of ethyl iodide with PTA dissolved in methanol. The crude product was recrystallized from methanol in 90% yield. ^{13}C nmr (D_2O) δ 7.6 (s), 48.4 (d), (J = 21.4 Hz), 54.9 (d), (J = 34.6 Hz), 61.1 (s), 72.2 (s), 81.1 (s). Calculated for $C_8H_{17}N_3PI$:C, 30.67; H, 6.07; I, 40.58. Found C, 30.37; H, 6.03; I, 40.36.

The benzyl chloride derivative of PTA was prepared similarly to the ethyl iodide and methyl iodide derivatives in 80% yield. ^{13}C nmr (DMSO-d^6) δ 45.2 (d), (J = 21.0 Hz), 51.3 (d), (J = 32.4 Hz); 61.2 (s), 69.2 (s), 78.4 (s), 126.0 (s), 128.9 (s), 130.1 (s), 132.9 (s).

Sulphur (1 g, 0.031 mole) and PTA (2 g, 0.0127 mole) were refluxed in 50 mL of water for 30 minutes. The solution was filtered and yielded 1.17 g (48.6% yield) after recrystallization from methanol.

Selenium (1.5 g, 0.019 mole) and PTA (2 g, 0.0127 mole) were refluxed in 50 mL of water for 1 hr. The solution was filtered and yielded 1.01 g (44.8% yield) after recrystallization from water. Calculated for $C_6H_{12}N_3PSe$: C, 30.51; H, 5.08. Found C, 30.42; H, 5.03.

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