The Oxidation of Organo-phosphines by Aqueous Alkali

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Summary The anaerobic oxidation of several water-soluble t-alkylphosphines by aqueous alkali results in the stoicheiometric evolution of hydrogen gas and the formation of the corresponding phosphine oxides.

WHEN aqueous alkaline solutions 0·1 N in tertiary phosphine of compounds **(1)**—**(7)**[†] were heated under reflux in 2N-sodium hydroxide, a stoicheiometric quantity of hydrogen gas was collected by water displacement in *ca.* 3 h. Each of these tertiary phosphines are water soluble, solubility being achieved by placing ω-carboxy- , hydroxy- , or aminoalkyl groups on phosphorus. (Usually tertiary aliphatic phosphines are extremely insoluble in aqueous media.)

$$[\mathrm{MeP}]_m\mathrm{P}[\mathrm{CH_2{\cdot}CH_2X}]_n$$

(1) X = CO_2H, $m = 0$, $n = 3$; **(2)** X = CO_2H, $m = 1$, $n = 2$; **(3)** X = CO_2H, $m = 2$, $n = 1$; **(4)** X = $CH_2{\cdot}OH$, $m = 0$, $n = 3$, **(5)** X = $CH_2{\cdot}OH$, $m = 1$, $n = 2$; **(6)** X = $CH_2{\cdot}OH$, $m = 2$; $n = 1$; **(7)** X = $CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, $m = 2$, $n = 1$.

The predominant organic product isolated in each case was the corresponding tertiary phosphine oxide (Equation 1).

$$\mathrm{R_3P + H_2O \xrightarrow{OH^-} R_3P{=}O + H_2} \qquad (1)$$

This alkaline oxidation is favoured thermodynamically by the extraordinary stability of the newly formed P=O bond (138 kcal mol^{-1}).[1] The dependence of the decomposition reaction on alkali concentration was easily demonstrated. When the hydroxide ion concentration of an aqueous solution, 0·1 N in methylbis-(2-carboxyethyl)phosphine, **(2)** was lowered from 2N to 10^{-5}N, no gas evolution was observed after 48 h reflux. Hydrogen evolution was not noticeably accelerated in the presence of added salt nor noticeably retarded in the presence of radical inhibitors (*e.g.*, hydroquinone and diphenylamine). In all cases the phosphine oxide obtained from the alkaline oxidation reaction was compared with a sample made by the peroxide oxidation[2] of the corresponding phosphine. Sodium ethoxide in ethanol was not an oxidizing medium. No gas evolution was observed for any of the phosphines **(5)**—**(7)**[†] in 2N-sodium ethoxide under reflux for 48 h.[‡]

The hydrogen evolution, the lack of radical inhibition, and the difficulty in observing any reaction with ethoxide in ethanol indicate that this oxidation differs from the well-known aerial oxidation of phosphines previously described by Buckler[3] and others.[4,5]

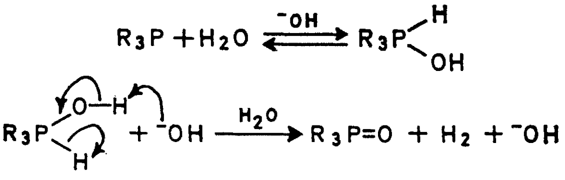
A possible mechanism for the oxidation is shown in the Scheme.

A similar scheme was suggested by Campbell and Stevens[6]

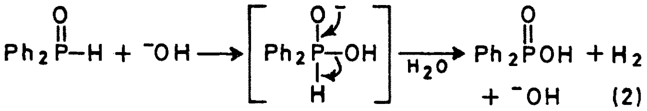
[†] All new compounds have satisfactory analytical and spectroscopic data.

[‡] Hydrogen evolution from **(2)**, **(4)**, and **(6)** in several alkaline alkyl-diol solvents, *e.g.*, $NaO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ in propane-1,3-diol has been observed. We have also measured the evolution of 2 equivalents of hydrogen gas from the anaerobic alkaline oxidation of bis-3-hydroxypropyl)phosphine to its phosphinic acid.

in which a hydride ion was expelled from phosphorus when ethoxide in ethanol was treated with secondary phosphine oxides. This oxidation was equally effective when aqueous hydroxide was used (Equation 2).



Scheme



$$Ph_2P(O)H + {}^-OH \longrightarrow [Ph_2P(O^-)(OH)H] \xrightarrow{H_2O} Ph_2P(O)OH + H_2 + {}^-OH \quad (2)$$

The observation that dimethyl-(ε-aminopentyl)phosphine, (**7**), reduced 2N-alkali to give a stoicheiometric quantity of hydrogen gas rules out the necessity for an intramolecular nucleophilic-assisted hydride displacement.

In order to deduce the requirements for the decomposition reaction the tertiary phosphine tris-(n-butyl)phosphine, with limited solubility in aqueous media, was tested. It failed to reduce 2N-alkali under reflux for 48 h.§ We had assumed that aromatic phosphines might be less prone to attack by alkali as their pK_a's are less than 2, in contrast to the strongly basic aliphatic phosphines (**1**)—(**7**), with pK_a values greater than 7. Tris-(*p*-hydroxyphenyl)phosphine and tris-(*o*-hydroxyphenyl)phosphine, however, both reduced alkali under the conditions described previously. The *ortho*-derivative was observed to generate the stoicheiometric quantity of hydrogen gas more rapidly than the *para*-derivative. We therefore have been unable to find any singular factor other than solubility in aqueous alkali which is necessary for the anaerobic oxidation of tertiary phosphines.

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§ Although this is a heterogeneous medium, Bu_3P is soluble in water to the extent of 0·1%. Attempted intermittent addition of ethanol or alkyl-diols to alleviate the solubility problem resulted in no observable gas evolution.

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