

parameters) was then refined, using 316 $h0l$ and $h1l$ reflections with a full-matrix least-squares program. At the present stage of refinement the conventional R factor is 7%. The fractional atomic parameters obtained and the interatomic distances are given in Tables 2 and 3.

A schematic representation of the structure is given in Fig. 1. It is seen that highly distorted octahedra and square pyramids are the basic structural elements. The $V(1)O_6$ and $V(2)O_6$ octahedra form zig-zag strings running in the b direction by edge-sharing. They are also joined by edge-sharing in the ac plane to double zig-zag ribbons extending along b . The $V(3)O_6$ and $V(4)O_6$ square pyramids form single zig-zag strings in the b direction. These strings are joined by corner-sharing among themselves and to the double zig-zag ribbons to form a three-dimensional framework. The vanadium-oxygen distances in the ribbons (Table 3) are in the range 1.60–2.40 Å (sixfold coordination), and the distances in the single chains are in the range 1.64–1.96 Å (fivefold coordination).

The structure of V_4O_{13} can alternatively be described by regarding it as composed of vanadium atoms exclusively in square-pyramidal coordination with oxygen, with an additional sixth oxygen weakly coordinated (bond type C , nomenclature according to Ref. 10), through the base of the pyramid and opposite to a short apex bond (bond type A). The short A bonds are in the range 1.60–1.66 Å (mean value 1.63 Å), and the basal B bonds are in the range 1.87–2.02 Å (mean value 1.94 Å). The sixth weak bonds (bond type C) are 2.23 and 3.00 Å, respectively. The square pyramid configuration is very common for tetravalent and pentavalent vanadium compounds. Among the many crystal structures¹⁰ having shown its presence, the average A bond length is 1.60 Å, and B bond length 1.91 Å. The C bond varies from 2.18 to 2.97 Å, or is sometimes absent altogether.

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Spin Trapping of Some Phosphorus-centered Radical Species

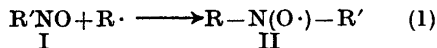
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Intermediate free radicals with the radical center located on a phosphorus atom are considered to be formed in many reactions of organo-phosphorus compounds, for example in the addition of primary and secondary phosphines to olefins.¹ The radical species considered to be present in the latter reactions, *i.e.* phosphinyl radicals, $R^1R^2\dot{P}$, have not been demonstrated so far by the technique of ESR spectroscopy. On the other hand, the ESR spectra of phosphoranyl radicals such as $R^1R^2R^3\dot{P}OR$ and $R^1R^2\dot{P}(OR)_2$, formed by the addition of *t*-butoxy radicals to phosphines, have been recorded at about -80° .^{2,3}

This note describes the trapping as nitroxide radicals of some phosphorus-centered radical species. The trapping of short-lived free radicals as stable nitroxide

radicals II utilizes the scavenger properties of nitroso compounds I (eqn. 1), and has now been applied to a large number of reactions.⁴⁻¹²



Free radicals were trapped as nitroxide radicals in a water solution of sodium phosphite, Na_2HPO_3 , containing the scavenger *t*-nitrosobutane. The spectrum consisted of 6 lines of equal intensity and appeared immediately after the sample had been irradiated *in situ* in the ESR cavity with UV light for a few seconds. An identical spectrum was obtained when H_2O was replaced by D_2O as the solvent. The yield of the radicals was increased when a few drops of H_2O_2 was added to the reaction mixture prior to irradiation.

The 6-line spectrum is consistent with the interaction of the unpaired electron with one ^{14}N and one ^{31}P nucleus, and the production of a nitroxide radical by the trapping of the radical ion, $\cdot\text{PO}_3^{2-}$, formed by the abstraction of the hydrogen atom bonded to the phosphorus atom of the parent ion, $\text{H}-\text{PO}_3^{2-}$. In the presence of hydrogen peroxide the abstraction of the hydrogen atom seems to be brought about by photochemically generated $\cdot\text{OH}$ radicals, but in the absence of H_2O_2 it is not clear whether the abstraction is caused by a photochemical scission of the $\text{H}-\text{P}$ bond, or by $\cdot\text{NO}$ or *t*-butyl radicals derived from the scavenger.*

* The $\cdot\text{PO}_3^{2-}$ radical ion has recently been trapped also on dissolving a γ -irradiated solid sample of sodium phosphite in a water solution of *t*-nitrosobutane.¹³

Similar 6-line spectra, but with somewhat different hyperfine splittings, were obtained with a number of phosphorus compounds by the abstraction of a hydrogen atom bonded to the phosphorus atom (Table 1). The radical species obtained with dimethyl phosphite could be obtained in a high yield in the absence of peroxide, and in a number of different solvents such as water, acetone, dimethyl sulphoxide and methylene chloride. Diethyl phosphite and dibutyl phosphite were also attacked by the photochemically generated $\cdot\text{OH}$ radicals with the abstraction of hydrogen atoms from the alkyl chain. In the case of dibutyl phosphite these radicals dominated over those formed by the abstraction of the hydrogen atom bonded to the phosphorus atom. However, radicals could be trapped from dibutyl phosphite which were exclusively produced by the abstraction of the hydrogen atom bonded to the phosphorus atom when peroxide was omitted, and especially when the nitroso scavenger was dissolved in dibutyl phosphite in the absence of other solvents.

The radicals trapped from phenyl phosphine gave rise to a 12-line spectrum with all lines of equal intensity (Fig. 1), indicating the trapping of $\text{Ph}-\dot{\text{P}}\text{H}$ radicals after the abstraction of one of the two hydrogen atoms bonded to the phosphorus atom of the parent compound.

A 6-line spectrum was obtained with tetramethylbisphosphine disulphide, $(\text{CH}_3)_2\text{P}(\text{S})-\text{P}(\text{S})(\text{CH}_3)_2$, after UV irradiation of the reaction mixture. Evidently, the phosphorus-centered radical species trapped in this case was formed by a homolytic cleavage of the $\text{P}-\text{P}$ bond.

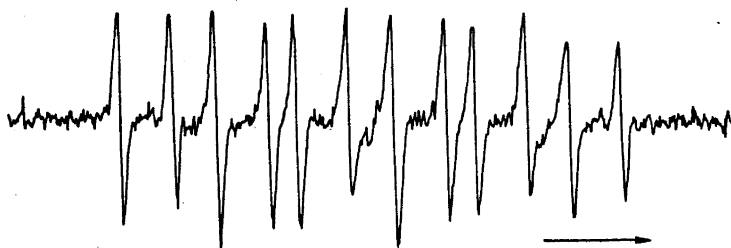


Fig. 1. ESR spectrum of the nitroxide radical $\text{Ph}-\text{P}(\text{H})-\text{N}(\text{O}\cdot)-\text{C}(\text{CH}_3)_3$, formed by trapping of the radical $\text{Ph}-\dot{\text{P}}\text{H}$ produced by UV irradiation of a solution of $\text{Ph}-\text{PH}_2$ in CH_2Cl_2 at room temperature. Scavenger: *t*-nitrosobutane.

Table 1. Splitting constants in gauss of the unsymmetric nitroxide radicals $R-N(O\cdot)-C(CH_3)_3$ formed from *t*-nitrosobutane and the radicals $R\cdot$ produced from some phosphorus-containing compounds at room temperature.

Parent compound	Solvent	a_N	a_P	a_H	Trapped radical $R\cdot$
Na_2HPO_3	H_2O	13.4	12.0		$\cdot PO_3^{2-}$
NaH_2PO_2	H_2O	12.3	10.6		$\cdot POH(O)^-$
$(CH_3O)_2PHO$	H_2O	10.3	13.8		$\cdot P(OCH_3)_2(O)$
$(EtO)_2PHO$	—	9.9	13.1		$\cdot P(OEt)_2(O)$
$(BuO)_2PHO$	—	9.9	13.1		$\cdot P(OBu)_2(O)$
$PhP(H)(OH)O$	H_2O	12.0	10.4		$\cdot P(Ph)(OH)(O)$
Ph_2PH	DMSO	13.2	11.4		$\cdot PPh_2$
$PhPH_2$	CH_2Cl_2	12.0	6.5	3.7	$\cdot P(H)Ph$
$(CH_3)_2P(S)-P(S)(CH_3)_2$	CH_2Cl_2	11.5	10.5		$\cdot P(S)(CH_3)_2$

No radicals of the type concerned could be trapped from compounds such as NaH_2PO_2 , $(CH_3)_3P$, or $(CH_3O)_3PO$.*

Untrapped phosphorus-centered radicals exhibit ^{31}P splittings about 600 gauss.^{2,3,14} These large splittings are caused by a $3s$ state contribution to the hybridized orbital containing the unpaired electron. The ^{31}P splittings of the nitroxides of this series are much smaller and were found to be between 6.5 and 13.2 gauss, only. It is evident that the large reduction of the ^{31}P splittings obtained on trapping phosphorus-centered radicals as nitroxides involves a drastic change of the interaction of the unpaired electron with the phosphorus nucleus. However, it is not known at present whether this change involves a very low spin density on the phosphorus atom in the nitroxides, or depends on a hybridization with a reduced contribution from the $3s$ state after the trapping of the radicals as nitroxides.

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* A small amount of a species exhibiting a 6-line spectrum identical to that obtained with Ph_2PH was observed with triphenyl phosphine indicating the production of $Ph_2P\cdot$ radicals by scission of a C—P bond.

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