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AUTOXIDATION OF TERTIARY PHOSPHITES

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This communication reports a study of attempted alkoxy-radical initiated autoxidation of a series of tertiary phosphites. The results have bearing on the question of potential reaction alternatives for phosphoranyl radicals which have been proposed[1] as possible intermediates in free radical reactions of trivalent organophosphorus.

For reactions of alkoxy radicals with trialkyl phosphites, Walling and Rabinowitz[2] have suggested the following oxidation sequence (R = Et, R' = t - Bu):

$$(1)\quad R'O\cdot + P(OR)_3 \xrightarrow{1} R'O\dot{P}(OR)_3 \xrightarrow{2} R'\cdot + OP(OR)_3$$

In the presence of oxygen, however, a greater than stoichiometric quantity of phosphate was formed and for the autoxidation process several additional reactions were suggested:[2]

$$R'\cdot + O_2 \xrightarrow{1} R'O_2\cdot$$

$$(2)\quad R'O_2\cdot + P(OR)_3 \xrightarrow{2} R'O\cdot + OP(OR)_3$$

$$R'O\cdot \xrightarrow{3} \text{etc., sequence (1)}$$

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We have attempted the autoxidation of 0.8M solutions of the following series of phosphites in refluxing chlorobenzene (130°) using di-t-butyl peroxide (DTBP) as initiator (molar ratio of phosphite to DTBP, 10 to 1). The reaction solutions were continuously saturated before and during heating with oxygen from a sparge tube.

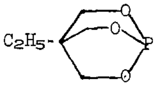
$(RO)_3P$

I, R = Et

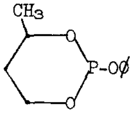
II, R = n-Bu

III, R = $ClCH_2CH_2$

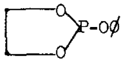
IV, R = ∅



V



VI



VII

$(C_2H_5O)_2PO$∅ VIII

Under these conditions phosphites I-III and V were completely consumed in 20-30 min., and the corresponding phosphates were isolated in 70-90% yields. In contrast no more than 10% of the phenyl phosphites, IV and VIII and 25% of VI and VII, underwent reaction during 2 hours under comparable conditions. On the other hand when azobisisobutyronitrile (AIBN) was used as initiator in refluxing benzene under otherwise similar conditions, phosphites I-VI were completely consumed to give high yields of the respective phosphates. (VII and VIII were not tested.)

It seems possible that with t-butoxy-radical initiation the phenyl phosphite oxidations fail because of chain termination through formation of the relatively stable phenoxy radical in an α-scission process (3) which competes successfully with the β-scission of step 2 of sequence (1).‡

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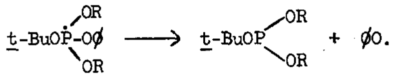
‡ The α-scission shown in (3) was also recently suggested by Walling and Pearson[5] as a possible explanation for the greater than stoichiometric consumption of phosphite in the competitive t-butoxy radical oxidation of a mixture of triethyl and triphenyl phosphites. Two unexpected peaks in the product gas chromatogram suggestive of a radical exchange were also noted.

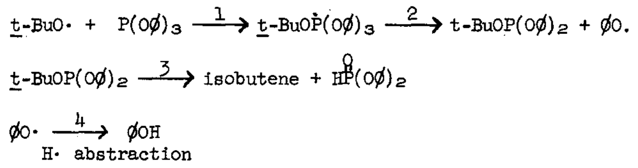
(3) 

$$(3)\quad t\text{-BuO}\dot{P}(OR)_2\text{-O}\phi \longrightarrow t\text{-BuOP}(OR)_2 + \phi O.$$

Phenoxy radicals thus formed would not be expected to continue the radical chain *via* sequence (1). With radicals from AIBN step 2 of sequence (1) apparently is more rapid (as would be predicted in view of the more stable $R'\cdot$ involved) and allows the chain to proceed resulting in oxidation of both phenyl and alkyl phosphites.

We find further support for reaction (3) from a product study of reaction of equimolar equivalents of triphenyl phosphite and *t*-butoxy radicals (from thermal decomposition of DTBP in chlorobenzene at 130°) in absence of oxygen. The reaction solution, 0.8M in phosphite and 0.4M in DTBP, was swept continuously with nitrogen, and material in the gas stream not returned to the reaction by an efficient icewater condenser was collected at Dry Ice temperatures and was shown by mass spectral analysis to be nearly pure isobutene, about 0.5 mole per mole of phosphite. It is most significant that *isobutane was totally absent*. Thus, isobutylene cannot arise from disproportionation of *t*-butyl radicals formed by α-scission.[‡] Large amounts of phenol were isolated from the reaction by distillation. In a similar reaction of a degassed and vacuum-sealed solution of these reactants in chlorobenzene (molar ratio of phosphite to *t*-butoxy radicals, 1.33) g.l.p.c. analysis of the products indicated, within experimental error, a 1:1 correspondence of moles phenol formed and phosphite reacted to moles of *t*-butoxy radical theoretically generated. *Triphenyl phosphate could not be detected by t.l.c.* A reaction scheme which incorporates reaction (3) and satisfies the above products and stoichiometry is:

[‡] *t*-Butyl radical disproportionation products were found from reaction of *t*-butoxy radicals with excess triethyl phosphite.[2]



$$\underline{t}\text{-BuO}\cdot + P(O\phi)_3 \xrightarrow{1} \underline{t}\text{-BuO}\dot{P}(O\phi)_3 \xrightarrow{2} t\text{-BuOP}(O\phi)_2 + \phi O\cdot$$

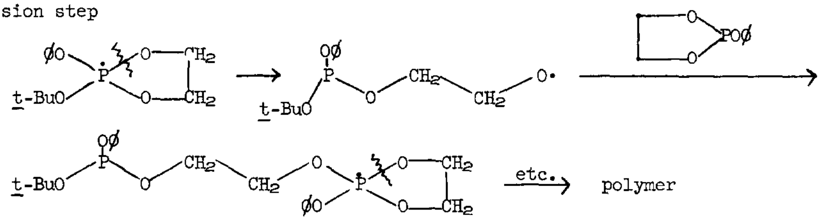
(4) $$\underline{t}\text{-BuOP}(O\phi)_2 \xrightarrow{3} \text{isobutene} + H\overset{O}{P}(O\phi)_2$$

$$\phi O\cdot \xrightarrow[\text{H}\cdot\text{ abstraction}]{4} \phi OH$$

Precedence for step 3 in sequence (4) is found in the facile formation of isobutene and di-*t*-butyl phosphite from tri-*t*-butyl phosphite.[4] The low yield of isobutene may result from inefficiency in the trapping procedure or from consumption of the olefin *via* subsequent free radical reactions. Evidence for the presence of diphenyl phosphite in the reaction product mixture includes: infrared comparison with known mixture of phenol, triphenyl phosphite and diphenyl phosphite; similar proton n.m.r. comparison--P-H coupling; formation of silver salt[5] with infrared spectrum corresponding to that of known material; and t.l.c. Relative peak heights in the n.m.r. indicated the presence in the products of 0.6-0.8 moles of diphenyl phosphite per mole of triphenyl phosphite reacted. This material was also isolated by fractional distillation in about 40% of the amount predicted by scheme (4). It is probable that some of the diphenyl phosphite formed was consumed either by addition to isobutene[6] or by free-radical phosphonation[7] of the aromatic solvent.

An alternative mechanism to explain these products involves hydrogen abstraction by t-butoxy radicals followed by transesterification exchanging the t-butanol thus formed for phenol and generating *t*-butyl diphenyl phosphite. However, some of the *t*-butoxy radicals would be expected to give methyl radicals and acetone, and the latter was not present in the products in appreciable amounts (by g.l.p.c.).

Reactions of phosphites VI and VII with stoichiometric equivalents of *t*-butoxy radicals also gave considerable amounts of phenol. In addition part of the product isolated from reaction of VII under these conditions was a rubbery phosphorus-containing polymer. A viscous polymeric product was also obtained from VI. These polymers may result from ionic routes -- perhaps phenol catalyzed. An intriguing alternative possibility, however, is the following free radical pathway which involves a ring-opening α-scission step



The effect of ring strain on α-scission in these reactions is being further evaluated in more-careful studies of reaction products.

Finally there is probably a significant relation between our results in attempted autoxidation of phosphites in oxygen with *t*-butoxy radical initation and those from UV light initiated oxidations of tertiary phosphites carried out by Griffin and Plumb[9] and also by Cadogan and coworkers[9]. Both reported facile oxidation of a variety of alkyl phosphites to the corresponding phosphates in very high yields but only partial oxidation of triphenyl phosphite in corresponding reaction times. Griffin did note, however, formation of triphenyl phosphate in 79% yield in an extended reaction. Both groups proposed a reaction sequence similar to (2).

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