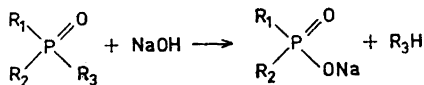


Decomposition of Triphenyl Phosphine Oxide in Alcoholic Alkaline Solution

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Phosphine oxides are compounds of high chemical stability, but it has been observed that when they are fused with alkali hydroxides they will lose their substituent radicals¹. This decomposition has recently been utilized by Horner *et al.*² as a method for preparation of phosphinic acids:



The greater the negativity of the substituents the easier are they lost during the fusion. The above authors observed the following order of stability: alkyl > phenyl > benzyl.

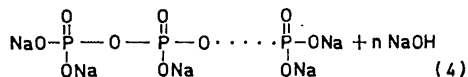
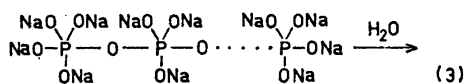
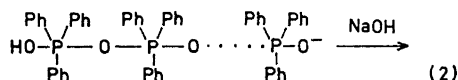
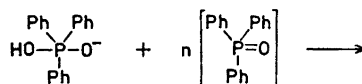
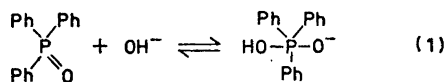
In this communication we wish to report the decomposition of triphenyl phosphine oxide under much milder condition than hitherto described.

When triphenyl phosphine oxide is boiled in an alcoholic solution of alkali hydroxide (*e.g.* 0.1 N NaOH and 0.2 M phosphine oxide in 96 % alcohol) during several hours, a gelatinous compound precipitates in the reaction flask. At the same time it is found that the hydroxide disappears from the alcoholic solution. No salt of phosphinic acid is found in the alcohol.

On treatment of the precipitate with water it decomposes into alkali hydroxide and insoluble inorganic alkali metaphosphate. No salt of phosphinic acid is found in the precipitate.

These observations are in accordance with the following reaction scheme.

This scheme postulates the formation of a pentacovalent intermediate as initiator of the chain process. Although Halmann and Pinchas³ found no exchange of phosphoryl oxygen in triphenyl phosphine oxide when boiled in ¹⁸O-enriched water, it is reasonable to expect that the exchange process is strongly catalysed by hydroxyl ions; Halman and Pinchas³ do not report



exchange studies in alkaline solution. During formation of the pentacovalent intermediate it seems most reasonable to expect a back side attack on phosphorus opposite to the phosphoryl group to give a trigonal bipyramidal structure with the three phenyl groups in the equatorial positions and the two oxygen atoms in the axial positions. The strong dipole of the phosphoryl group is expected to favour this configuration. In order to explain that diphenyl phosphinic acid is not formed we must assume that release of phenyl groups from the monomeric pentacovalent state requires higher energy than the coupling of the negatively charged oxygen with another phosphine oxide molecule. Since the sodium metaphosphate formed is totally insoluble in water the chains must consist of a great number of phosphate units.

It seems reasonable to assume that the displacement of the phenyl groups by hydroxyl ions from the polymer chains follows immediately upon the polymerisation due to the fact that there is no indication of organic material in the precipitate formed during the reaction.

Horner *et al.*² have shown that fusion of triphenyl phosphine oxide with sodium hydroxide quantitatively gives the monomeric product, sodium diphenyl phosphinate. The difference in behaviour can be explained if the first step in the fusion

process consists of a quantitative formation of the pentavalent intermediate, the decomposition of which can only give monomeric product. Additional evidence for this interpretation is found in the non-proportionality between phosphine oxide decomposition and the hydroxyl concentration in alcoholic solution. Thus, 2 N KOH in 96 % alcohol gives after 48 h boiling 30 % decomposition of a 0.2 M triphenyl phosphine solution as compared with 18 % under the same conditions in 0.2 N NaOH. In 70 % alcohol 0.1 N NaOH gives after only 24 h boiling 45 % decomposition of 0.2 M triphenyl phosphine oxide solution. In the latter case some sodium metaphosphate crystallized directly from the reaction solution. Apparently a greater amount of water in the alcohol will favour the metaphosphate formation from the pentavalent polymer (step 3). An equivalent amount of hydroxyl ions will then be liberated which can decompose additional amounts of triphenyl phosphine oxide.

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Eosine Sensitized Formation of Photo-Radicals in Liquid Solutions

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It has been established that transient free radicals are formed in the light-induced reaction between levopimaric acid and eosine¹. In connection with this work other reactions sensitized by eosine were studied by the technique of electron spin resonance (ESR). Some of the results are to be reported here. The experimental arrangements were the same as described earlier¹.

When a solution of eosine and ascorbic acid in pyridine was irradiated by visible light *in situ* at room temperature, Bubnov *et al.*² found free radicals by the ESR-technique. The dye sensitizer was considered to be excited to a triplet state when absorbing radiant energy. Subsequently, a hydrogen atom was assumed to be transferred from ascorbic acid to the excited dye molecule. The radical observed was believed to be a semiquinone of eosine, as the ESR-spectrum exhibited a three-line structure with a hyperfine splitting of 4.6 gauss which was considered to be due to the interaction of an unpaired electron with the two hydrogen atoms located on carbon atoms 1 and 8 in the xanthene nucleus of the eosine molecule.

This reaction has been studied in this laboratory using pyridine or ethanol as a solvent. However, an identical three-line spectrum is obtained also when the sodium salt of fluorescein or 4,5-diodofluorescein is substituted for eosine (the sodium salt of 2,4,5,7-tetrabromofluorescein) in the reaction with ascorbic acid. As there are six hydrogens in fluorescein, and four hydrogens in 4,5-diodofluorescein available for interaction with the unpaired electron as compared with two hydrogens in eosine, it seems difficult to correlate the three-line structure of the spectra obtained with a semiquinone radical derived from the dye molecule.

Photo-induced radicals have been observed at room temperature in analogous systems containing eosine, in which ascorbic acid has been replaced by other substances using ethanol or pyridine as a solvent. Thus, a three-line spectrum which could not be distinguished from that observed for the reaction of ascorbic acid, was obtained in the case of such widely different substances as benzaldehyde, 1,1-diphenylhydrazine, pyrrole, *p*-toluenethiol and xanthotoxin. When the light is turned on radicals appear immediately and the concentration remains constant until the light is turned off. The reaction rates are certainly much faster than those reproducible with true fidelity by the recorder used.

Considering the three-line ESR-spectrum a simple interpretation does not seem to be possible in terms of a radical derived from the dye sensitizer, the substrate or the solvent. In a recent study of photo-induced reactions similar to those here considered Schenck and Wolgast³ assume that the radical exhibiting the three-line spectrum is an addition complex built up between