

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

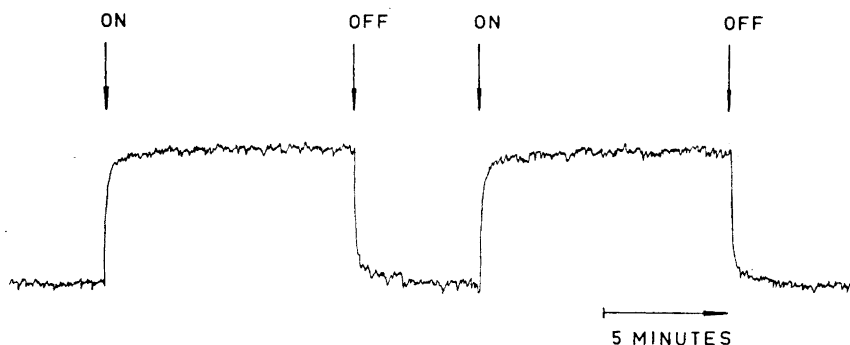


Fig. 1. Photo-induced radicals from a 10^{-2} M solution of 1,4-dihydroxybenzene in H_2O . Eosine concentration 10^{-3} M. The relative radical concentration is recorded as a function of time. The sample was irradiated *in situ* by light from a xenon lamp filtered through a 50 mm layer of 10% $CuSO_4$ in H_2O . Vertical arrows mark light "on" and "off".

the excited sensitizer and the substrate. Closer details about this complex seem to be lacking.

Although the three-line spectrum is a common phenomenon in photo-reactions sensitized by eosine, other substances have been found which give rise to radicals definitely connected with the substrate molecules. Thus, 1,4-dihydroxybenzene in ethanol or water exhibits the characteristic five-line spectrum of the *p*-semiquinone radical. The radicals appear and disappear synchronously when the light is turned on and off

(Fig. 1). An identical spectrum and the same kinetic behaviour were observed also when 1,4-dihydroxybenzene was replaced by *p*-benzoquinone. No radicals could be detected when *p*-dimethoxybenzene was used as a substrate.

N,N-Diphenylamine dissolved in ethanol or pyridine gives rise to photo-induced radicals when sensitized by eosine. The radical concentration increased to a maximum value and then decreased almost to zero in a few minutes. It was found that the decay stopped when the light was turned off as

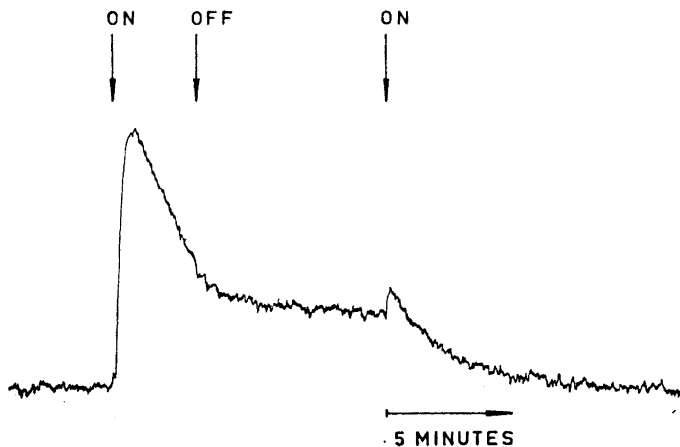


Fig. 2. Photo-induced radicals from a 10^{-2} M solution of *N,N*-diphenylamine in pyridine. Eosine concentration 10^{-4} M. For other details see legend of Fig. 1.

shown in Fig. 2. Evidently, the radicals are both formed and destroyed by the action of light. The ESR-spectrum, recorded in the dark immediately after the radical concentration had reached the maximum value, exhibited a hyperfine structure, consisting of at least 37 lines in three main groups. The spectrum was nearly identical with that reported by Hoskins ⁴ for the stable radical obtained when diphenylamine was oxidized by molecular oxygen in a hot mixture of toluene and alkaline ethanol. This radical was considered to have the structure $(C_6H_5)_2NO\cdot$. It may be suggested that the hydrogen attached to the nitrogen atom of diphenylamine is removed in the photo-induced reaction here described yielding the radical $(C_6H_5)_2N\cdot$.

An ESR-spectrum probably derived from the substrate molecule was obtained in the eosine sensitized reaction of phenothiazine. Due to the instability of the radicals both when the sample was irradiated and when kept in the dark, it was impossible to obtain a complete spectrum under high-resolution conditions. It was observed, however, that there were three main lines separated by about 9.5 gauss, very probably produced by the interaction of the unpaired electron with the nitrogen atom of phenothiazine. The main lines exhibited a splitting into a large number of more or less completely resolved lines. Although the ESR-spectrum does not give precise information, it is believed that the hydrogen atom attached to the nitrogen atom is removed in the radical forming process. To get photo-induced radicals from phenothiazine the presence of this hydrogen seems to be essential, as it was found that no radicals could be detected when N-methylphenothiazine was used as a substrate. However, the radical reactions of unsubstituted phenothiazine are rather complex. Under certain conditions photo-radicals are formed even without eosine as a sensitizer ⁵.

Thus, the reaction mechanism of N,N-diphenylamine and phenothiazine probably involves an irreversible homolytic extraction of a labile hydrogen. The radicals are derived from the substrate molecules and are present even after the excitation of the sensitizer has ceased. In some other reactions it has been suggested that an addition complex ³ is formed between the excited sensitizer and the substrate. This complex decays rapidly after the excitation has ceased, in some cases obviously reversibly as seen from the kinetic behaviour of

1,4-dihydroxybenzene where the light-induced reaction can be repeated an indefinite number of times.

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Synthetic Ascorbigen as a Vitamin C Source for Guinea Pigs and Man

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It was found in this laboratory that 3-hydroxymethylindole (II) is formed during the enzymic splitting of glucose and sulfate from the newly discovered thioglucoside, glucobrassicin (I), present in cabbage plants and isolated in pure form ^{1,2}. 3-Hydroxymethylindole reacts non-enzymically with the ascorbic acid present in cabbage to form the compound known as ascorbigen (III) ³.

