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PHOTO-SENSITIZED OXIDATION OF 0,0-DIMETHYL, 0-4-NITRO-m-TOLYL PHOSPHOROTHIOATE BY SINGLET OXYGEN

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Methylene blue-sensitized oxidation of 0,0-dimethyl,0-4-nitro-m-tolyl phosphorothioate (fenitrothion) by singlet oxygen has been carried out in methanol. Photo-product has been isolated and characterized as fenitrooxon. A tentative mechanism for the reaction has been proposed involving participation of singlet oxygen.

INTRODUCTION

The photochemical reactions of organophosphates are limited to phosphates such as imidan[1], dursban[2] and guthion[3] but the mechanism of their degradation is still obscure. The presence of sulphur atom in most of the important phosphates decides the degradation pathways[4]. Degradation of fenitrothion from cow fed diets[5], the kinetic constants for the inhibition of acetylcholinesterase by sumioxon (fenitro- oxon)[6], effects of aliphatic acids on metabolism and potency of Fenitrothion[7] have been studied but negligible attention has been paid for the photosensitized oxidation of Fenitrothion by singlet oxygen, and, therefore, the present work was undertaken.

EXPERIMENTAL

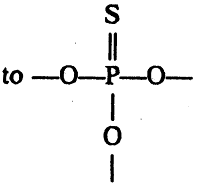
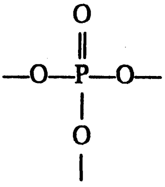
1,4-Diazabicyclo 2,2,2 octane (DABCO), lead acetate, 1,4-dioxane, methylene blue, methanol (BDH) were used except fenitrothion which was of technical grade. A 200 watt tungsten lamp was used for irradiating the reaction mixture. The infra-red radiations were cut off by a water filter. The concentration of methylene blue was 2.0×10^{-6} M in reaction mixture, which contains methanolic solution of fenitrothion (5% V/V). The reaction mixture was then aerated in the presence of light. The progress of the reaction was followed by TLC at regular intervals using solvent system n-butanol : ammonia = 80 : 20 (v/v).

A separate liquid layer was observed after 5 hrs of irradiation along with some turbidity in the reaction mixture. It was filtered and a yellow solid mass was obtained as residue. It was identified as sulphur[8] (m.pt. 118°C). The yellow crystals were treated with aqueous NaOH and then a drop of $KMnO_4$ was added, which rapidly gets decolorized. It clearly indicates that thiosulphate has been formed in the solution. Further, when this solution was treated with lead acetate, a black precipitate of lead sulfide was obtained. It confirmed the presence of sulphide ions and hence sulphur in the solution. It was observed that filtrate consisted of two separate layers. The adsorbed methylene-blue was removed from the reaction mixture (filtrate) using activated charcoal. The two layers were separated by a separating funnel. The upper layer was found to contain the photo-product while the lower layer contained the parent compound itself. The liquid photo-product was purified by fractional distillation (yield 12.5%). It gives negative test for sulphur.

RESULTS AND DISCUSSION

The boiling point of fenitrothion was 144°C(d) and that of the photo-product was 203°C(d). Quantitative elemental analysis of the photo-product gave following results:

Found:	$C = 41.20\%$;	$H = 4.43\%$;	$N = 5.25\%$
Calculated for $C_9H_{12}NO_6P$:	$C = 41.37\%$;	$H = 4.59\%$;	$N = 5.36\%$

Fenitrothion and its photo-product both were hydrolysed with alkali and the hydrolysed solution of photo-product gave positive test for phosphate, while in case of parent compounds, phosphate was found to be absent. This indicates that P=S bond was the site of attack during photo-oxidation. The photo-product has been identified as fenitro-oxon by comparison of IR spectra of fenitrothion with that of its photo-product. A characteristic band in case of fenitrothion appears at 824 cm^{-1} due to  $-\mathrm{O}-\overset{\overset{\textstyle \mathrm{S}}{\|}}{\underset{\underset{\underset{\textstyle |}{\textstyle \mathrm{O}}}{|}}{\mathrm{P}}}-\mathrm{O}-$ group[9] which is absent in the IR spectrum of the photo-product, thus indicating that this group was the site of photo-oxidation. A new band was found to be present at 1266 cm^{-1} in IR spectrum of the photo-product which is characteristic for the presence of  $-\mathrm{O}-\overset{\overset{\textstyle \mathrm{O}}{\|}}{\underset{\underset{\underset{\textstyle |}{\textstyle \mathrm{O}}}{|}}{\mathrm{P}}}-\mathrm{O}-$ group[10]. This suggests that an oxygen atom has entered the molecule from singlet molecular oxygen at the cost of a sulphur atom. The NMR spectra of both fenitrothion and fenitro-oxon were found identical, so these were not of much use from structure elucidation point of view.

The control experiments were carried out and it was found that the presence of dye, light and oxygen all the three components is essential as no product is formed when any one out of the three was removed. The participation of singlet molecular oxygen was confirmed by the decrease in the yield of the product when the reaction was carried out in presence of singlet oxygen scavengers[11-16]. Results are summarized in Table 1.

TABLE 1
EFFECT OF SINGLET OXYGEN SCAVENGERS

[Methylene blue] = 2.0×10^{-6} M

[Scavenger] = 1.0×10^{-6} M

Time of irradiation = 6 hours

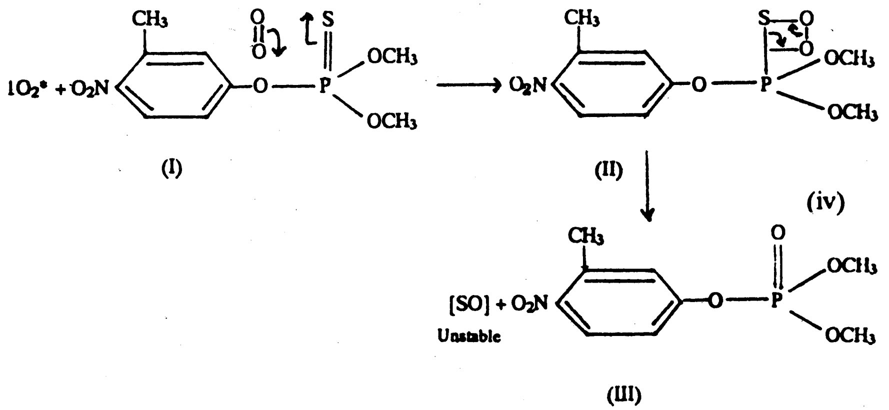
Scavenger	Yield %
—	12.5
Nickel chloride	0.3
Cobalt chloride	0.2
DABCO	Nil
α-Tocopherol	0.1

It is clear from Table 1 that the yield of the product is greatly reduced in the presence of singlet oxygen scavengers. This confirms that the active oxidising species in this reaction was singlet molecular oxygen. Information gained from the experimental observations leads to the following tentative mechanism for the photo-sensitized oxidation of fenitrothion by singlet molecular oxygen. The generation of singlet molecular oxygen from ground state oxygen involves three steps. The first step involves the excitation of the dye from its ground state to electronically excited singlet state, which is initiated by the absorption of light radiations of certain wavelengths by the dye in its ground state. Then it relaxes to its triplet state. Then this triplet state transfers its energy to the ground state oxygen molecule converting it into singlet molecular oxygen. Now, singlet molecular oxygen attacks the P=S bond in fenitrothion (I) to form a dioxetane like species (II) which decomposes to give fenitro-oxon (III) as the major product.

$$ {}^1D_0 \xrightarrow{h\nu} {}^1D_1 \qquad \text{(i)} $$

$$ {}^1D_1 \xrightarrow{ISC} {}^3D_1 \qquad \text{(ii)} $$

$$ 3O_2 + {}^3D_1 \longrightarrow {}^1D_0 + {}^1O_2^* \qquad \text{(iii)} $$



The formation of such dioxetane and its decomposition to give sulphur monooxide is in agreement with earlier observations[17]. Sulphur monooxide is a very short lived species and it disproportionates to give sulphur and sulphur dioxide[18].

$$3SO \rightarrow S_2O + SO_2 \qquad (v)$$

$$2S_2O \rightarrow 3S + SO_2 \qquad (vi)$$

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