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Photo-Oxidation of O-O-Dimethyl-O-4-Nitro-*m*-Tolyl Phosphorothioate (Fenitrothion) by Uranyl Acetate

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Reaction of fenitrothion with uranyl acetate was carried out using methanol as a solvent in presence of a perchloric acid. A liquid layer was isolated and characterized as fenitro-oxon by physical, chemical and spectral methods. A quantitative mechanism has been proposed for this reaction.

INTRODUCTION

The environmental fate of pesticides is a matter of great interest and concern. Many advancements have been made in the fields of metabolic processes of pesticides,[1,2] and their effects on plants, animals, men and the environment. Many modern pesticides contain sulphur atoms, which offer reactive sites for environmental degradation processes including photolysis, photo-oxidation and sensitized photo-oxidation.[3] The uranyl ion UO_2^{2+} is strong photo-oxidant and may help in understanding its photo-chemical behaviour with organophosphate pesticides. In natural waters minute quantities of uranium are believed to exist as uranyl carbonato complexes and the source of photo-excitation is sunlight.[4] The study of the photochemistry of organo-phosphate pesticides has been limited mainly to the name brand phosphates such as imidan,[5] Durshan[6] and Guthion[7] and in general little has been done to establish the mechanism of degradation. Information on UO_2^{2+} photosensitized oxidation of organophosphates is lacking. Most of the phosphates contain at least one sulphur atom; their presence dominates the degradation pathway. Two major types of product have been reported, the oxygen analogs in which the only structural change is the replacement of sulphur by oxygen resulting from $\geqslant P=S$, $\geqslant P=O$ and $>C=O$ bond cleavages,[8] and in others oxygen attack on sulphur atoms to give sulphoxides[9] as major product. In view of these divergent opinions it was considered of interest to undertake the little investigation with a view to throw some more light on the mechanism of these oxidation reactions.

EXPERIMENTAL

Fenitrothion (technical grade, b.p. 144°C) (O-O-dimethyl, O-4-nitro-*m*-tolyl phosphorothioate), uranyl acetate (BDH), perchloric acid (E. Merck) and methanol (BDH) were used. Double distilled methanol was used to prepare all the solutions. Fenitrothion (2.21 g) was dissolved in methanol, solutions of uranyl acetate (20 mL 0.01 M) and perchloric acid (6 mL, 0.1 M) were added to it and total volume was made 100 mL. The concentration of different ingredients in the reaction mixture was fenitrothion 0.08 M, uranyl acetate 0.002 M and perchloric acid 0.006 M. The pH of the solution was determined by Systronics 335 digital pH meter and was found to be 2.0. The solution was irradiated with light source (tungsten lamp, 3 × 200 W, Sylvania). The distance between the lamps and reaction vessel was 25 cm; water filter was placed between the light source and reaction vessel to cut off infra-red radiation. Oxygen gas (2 lit. $\min^{-1}$) was continuously bubbled through the reaction mixture. This served two purposes; firstly, regeneration of U(VI) from U(IV) and secondly, continuous stirring of the reaction mixture. The progress of reaction was observed with the help of TLC at every 2 h interval using solvent system *n*-butanol : ammonia 80 : 20 (v/v). Infra-red spectra were scanned on Perkin-Elmer Grating 377 Spectrophotometer; elemental analyses were carried using Carlo-Erba-1106 Automatic Analyzer.

A separate liquid layer was observed after 4.5 h of irradiation along with some turbidity. It was filtered after completion of reaction; a yellow solid mass was obtained as residue. It was identified as sulphur[10] by usual tests. It was observed that the filtrate consisted of two separate liquid layers, which were separated by a separating funnel. The lower layer contained the parent compound while photo-product came with the upper layer. The photo-product was purified by fractional distillation, b.p. 202°C, yield 19.23%. Variations in the concentration of substrate, uranyl acetate, and perchloric acid were performed.

VARIATION OF THE CONCENTRATION OF THE SUBSTRATE
IN REACTION MIXTURES[1]

$[UO_2^{2+}] = 0.002$ M Irradiation time = 5 h $[H^+] = 0.006$ M

Concentration of substrate (S)	% Reaction
0.16 M	11.99
0.11 M	12.09
0.08 M	19.23
0.05 M	23.07
0.04 M	24.27

VARIATION OF THE CONCENTRATION OF THE UO_2^{2+} IN REACTION MIXTURE.

Substrate = 0.08 M Irradiation time = 5 h $[H^+] = 0.006$ M

Concentration of $[UO_2^{2+}]$	% Reaction
0.0005 M	12.09
0.0010 M	14.42
0.0020 M	19.23
0.0030 M	24.03
0.0040 M	26.44

EFFECT OF CONCENTRATION OF [H^+] ION

Substrate = 0.08 M Irradiation time = 5 h [UO_2^{2+}] = 0.002 M

Concentration of [H^+]	% Reaction
0.002	10.09
0.004	14.14
0.006	19.23
0.008	24.27
0.01	25.01

The control experiment was also performed,[11] the reactions were carried out in presence of

(i) Uranyl ion and oxygen (no exposure of light)
(ii) Light and oxygen (no uranyl ions were added)
(iii) Uranyl ions and light (no oxygen was bubbled)

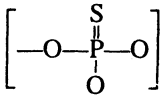
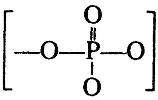
No photo product was formed in the first two cases and the yield was very low in the third case, so it may be concluded that uranyl ions and light are necessary for the photo-oxidation of fenitrothion and oxygen is required to regenerate U(VI) from U(IV) and hence increasing the yield of photo-product[12, 13]. The presence of acid assists in the decomposition of substrate U(VI) exciplex into the photo-product and U(IV)[14].

RESULTS AND DISCUSSION

The photo-product has been characterised as fenitro-oxon. The boiling point of fenitrothion is 144°C and that of the photo-product is 202°C. Quantitative elemental analysis of the photo-product gave the following results:

Found: C = 40.20%, H = 4.33%, N = 5.25%, S = 0.0%

Calculated for $CaH_{12}NO_6P$: C = 41.37%, H = 4.59%, N = 5.36%, S = 0.0%.

From the data obtained above it seems that photo-product has no sulphur. The absence of sulphur in the photo-product was further confirmed by sulphur estimation. Fenitrothion and its photo-product both were hydrolysed with alkali and the hydrolysed solution of the photo-product gave positive test for phosphate, which implies that P═S bond has been the site of attack in photooxidation, while in case of parent (fenitrothion), phosphate was found to be absent. The photoproduct has been identified as fenitro-oxon by comparision of IR spectra of fenitrothion with that of its photo-product. The bands were found at 3080, 3060, 2920, 2820, 1570, 1330, 1150, 1050 and 725 cm^{-1}. Moreover, in case of fenitrothion, a characteristic bond appears at 824 cm^{-1} due to  $\left[-O-\overset{\overset{S}{\|}}{\underset{\underset{O}{|}}{P}}-O\right]$[15] group which is absent in the IR spectrum of the photo-product thus indicating that this group indeed is the site of photo-oxidation. A new band was found at 1266 cm^{-1} in IR spectrum of the photoproduct of  $\left[-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}-O\right]$[16] group.

This suggests that an oxygen atom has entered the molecule from UO_2^{2+} at the cost of a sulphur atom. The NMR spectra of both fenitrothion and fenitro-oxon were found identical.

The information gained from the experimental data leads to the following mechanism which explains the observed results are quite satisfactory and is in conformation with the mechanism proposed by earlier workers.

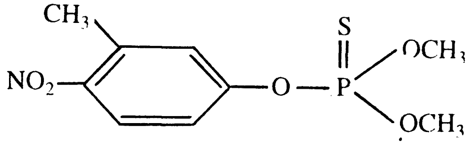
$$V + UO_2^{2+} \overset{h\nu}{\rightleftharpoons} [V \ldots UO_2^{2+}]$$

$$[V^{+} \ldots\ldots UO_2^{2+}] \xrightarrow{H^{+}, UO_2^{2+}} K + UO^{2+} + S$$

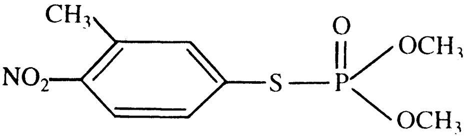
$$2UO_2^{2+} + {}^{1}O_2 \xrightarrow{h\nu} 2UO_2^{2+}$$

$$S + UO_2^{2+} \xrightarrow{h\nu} SO_2 + 2UO^{2+}$$

V =



S =



Mechanism of sensitized photo-oxidation of fenitrothion by uranyl ions.

First exciplex is formed between fenitrothion and excited uranyl ion which readily decomposes into fenitro-oxon, sulphur and UO^{2+}. It was shown that the deactivation of UO_2^{2+} starts from bimolecular collision between UO_2^{2+} and fenitrothion; an exciplex $[UO_2^{2+} \ldots . O]$ is formed. This exciplex is subject to intramolecular electron transfer from the fenitrothion to UO_2^{2+} to form an unstable intermediate $(UO_2^{+} \ldots O)$ which decomposes to UO^{2+} and fenitro-oxon. A part of the sulphur is converted into SO_2 by its reaction with excited uranyl ions. UO^{2+} so produced reacts with molecular oxygen in presence of light giving UO_2^{2+} and hence maintaining a steady state concentration of UO_2^{2+}.

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