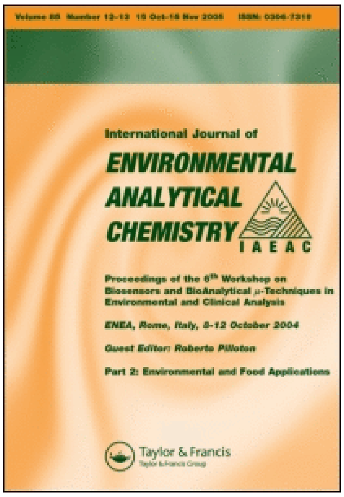

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ELECTROCHEMICAL BEHAVIOR OF METHYLPARATHION UNDER UV IRRADIATION

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The electrochemical behavior of methylparathion under UV irradiation was monitored by polarography in an aqueous medium (pH 6.5) at 254 and 366 nm, and the effects of atmospheric oxygen and TiO_2 on methylparathion were also looked at. Dissapearance of the methylparathion and appearance of two major electroactive degradation products were observed. The reaction rate constants for the process ranged from 3.55×10^{-5} to 5.69×10^{-5} s^{-1}, and the reaction showed pseudo-first-order kinetics. The methylparathion transformation did not depend on the experimental conditions. Spectroscopic and electrochemical data suggest the presence of p-nitrobenzoic acid as a common electroactive product.

Keywords: methylparathion; polarography; UV irradiation; organophosphorus pesticides; nitroaromatic compounds degradation

INTRODUCTION

There are a number of characteristics of organophosphorus pesticides, including their persistence[1], degradation and elimination[2–3], genetic effects on diverse organisms[4–6], and effects on people's health[7] that are of social and scientific interest. These characteristics involve many chemical reactions, and thus analytical chemistry plays an important role, not only in the detection and quantification of various compounds, but also in understanding their interaction with the environment[8–13]. Methylparathion *(Dimethyl-O-(4-nitrophenyl) phosphorothioic*

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acid) is an organophosphorus pesticide in use around the world today[3,7,14-17]. Previous experiments concerning transformation of methylparathion in water have been carried out in our laboratory employing electrochemical methods. Hydrolysis of this pesticide in an alkaline aqueous medium[10] and its electrochemical elimination in water over a wide range of pH values[11] were studied. Electroactive products p-nitrophenol, hydroxylamine, and amine derivatives were identified under various experimental conditions. Reaction mechanisms and possible products were proposed, information that is useful for understanding the fate of the pesticide in an aqueous medium. In this paper, which compliments studies of the transformation pathway of methylparathion in water, the electrochemical behavior of the pesticide in an aqueous solution was monitored by differential pulse polarography under UV irradiation to obtain additional data concerning its degradation in water (where redox properties occur).

EXPERIMENTAL

Apparatus

UV lamps used were a Black-ray Ultraviolet model UVG-11, 4 watts, 254 nm and a Mineralight Ultraviolet model UVGL-58, multiband, 366 and 254 nm. The apparatus consisted of a Metrohm 693 VA Processor with a 694 VA Stand. A static mercury drop electrode (SMDE) was used as working electrode, a platinum wire as auxiliary electrode and Ag°/AgCl redox system as reference electrode. pH measurements were made with a Corning potentiometer model pH/ion to Analyzer 350 with combined glass electrode.

Reagents

1×10^{-2} mol dm^{-3} stock solution of methylparathion (> 95%) was prepared by dissolving the solid product (Monsanto) in acetone. From this stock solution a methylparathion solution (5×10^{-5} mol dm^{-3}) was prepared by adding 0.1 mol dm^{-3} $LiClO_4$ aqueous solution. Other chemical reagents were of analytical grade and were used without later purification. The gas used for eliminating the oxygen in the solutions was nitrogen (purity 99.99%). All experiments were carried out at 25 ± 2 °C and pH 6.5 ± 0.2 (the natural pH of the studied solutions).

Procedure

Methylparathion absorbs short wavelength ultraviolet light ($\lambda < 290$ nm) but not long wavelength ultraviolet light ($\lambda > 290$ nm). Experimental conditions were:

1) Irradiation under nitrogen atmosphere ($\lambda = 254$ nm)

2) Irradiation under oxygen atmosphere

a) Only oxygen atmosphere ($\lambda = 254$ nm)

b) In the presence of metallic mercury ($\lambda = 254$ nm)

c) In the presence of TiO_2 ($\lambda = 366$ nm)

Irradiation of the methylparathion solutions under oxygen atmosphere was made after saturating them with atmospheric air. The irradiation under nitrogen atmosphere was done after bubbling nitrogen gas into the solution. The majority of the experiments were carried out during 480 minutes, but 900 minutes of irradiation were required to eliminate 90% of methylparathion. Monitoring intervals were 5 minutes at the start and became progressively longer, increasing to an hour towards the end of the experiment. The monitoring procedure was as follows: N_2 was bubbled for 10 minutes into a 25 mL of a 5×10^{-5} mol dm^{-3} methylparathion solution in the measurement cell, after which the corresponding polarogram was recorded. Pulse amplitude was 50 mV and the scan rate was 6 mV s^{-1}. In order to work with the simplest medium, all experiments were carried out at the natural pH of the studied solutions (6.5 ± 0.2).

RESULTS AND DISCUSSION

Irradiation under nitrogen atmosphere

After the first 10 minutes of irradiation, a continuous decrement in the signal of the pesticide was observed. At 300 minutes, the methylparathion signal had diminished by 70%, with some poorly defined signals appearing at a potential range from –0.4 to –0.9 V (Figure 1). Degradation of methylparathion occured at the greatest rate during the first 40 minutes of irradiation, when 50% of the pesticide disappeared, after which time it diminished only an additional 20%.

Irradiation under oxygen atmosphere

a) Only oxygen atmosphere

After 50 minutes of irradiation, change in methylparathion concentration was very slow, requiring approximately 900 minutes to degrade 90% of methylparathion. Two main products were observed at –0.34 V (product A) and at –0.85 V (product B) (Figure 2).

Peak current intensity (ip) of products was smaller than initial ip of methylparathion, which indicates either that there was not quantitative conversion of the

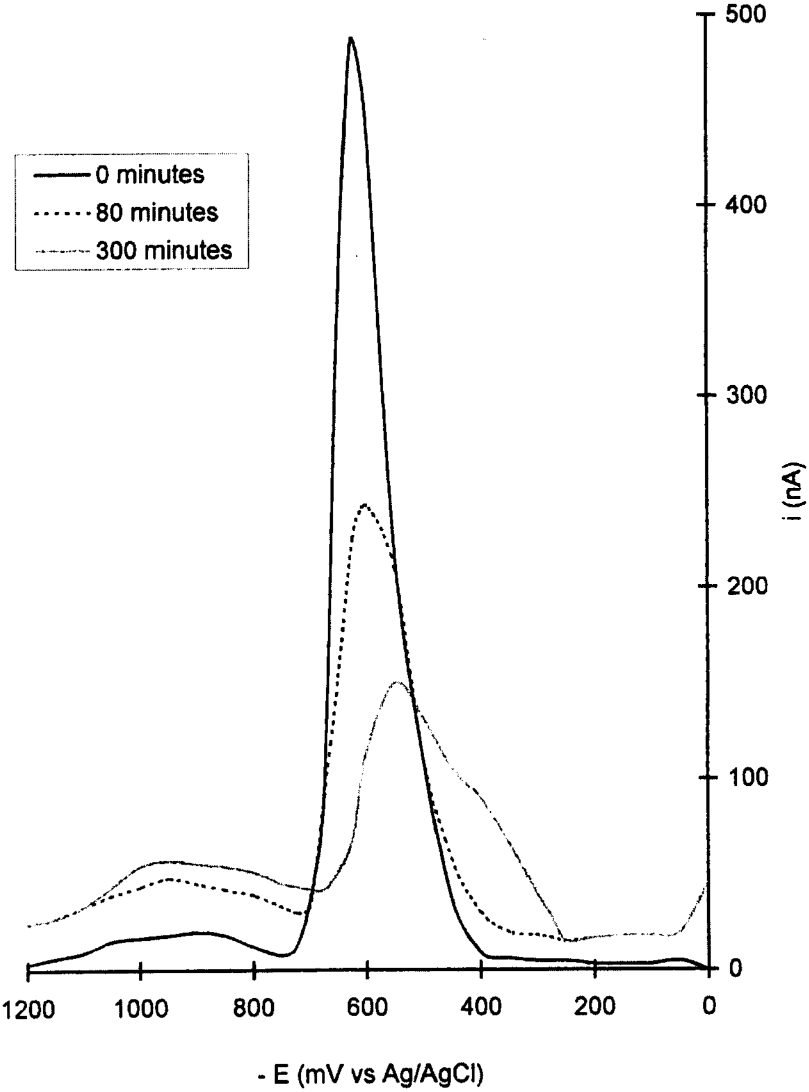


FIGURE 1 Polarograms of methylparathion (MP) recorded during its UV irradiation under nitrogen atmosphere. [MP] = 5×10^{-5} mol dm^{-3}, $\lambda = 254$ nm

pesticide to these products specifically or that the number of electrons involved in the reduction of such products is smaller than those interchanged in the reduction of methylparathion (this later number being four electrons). It is possibly a combination of both factors.

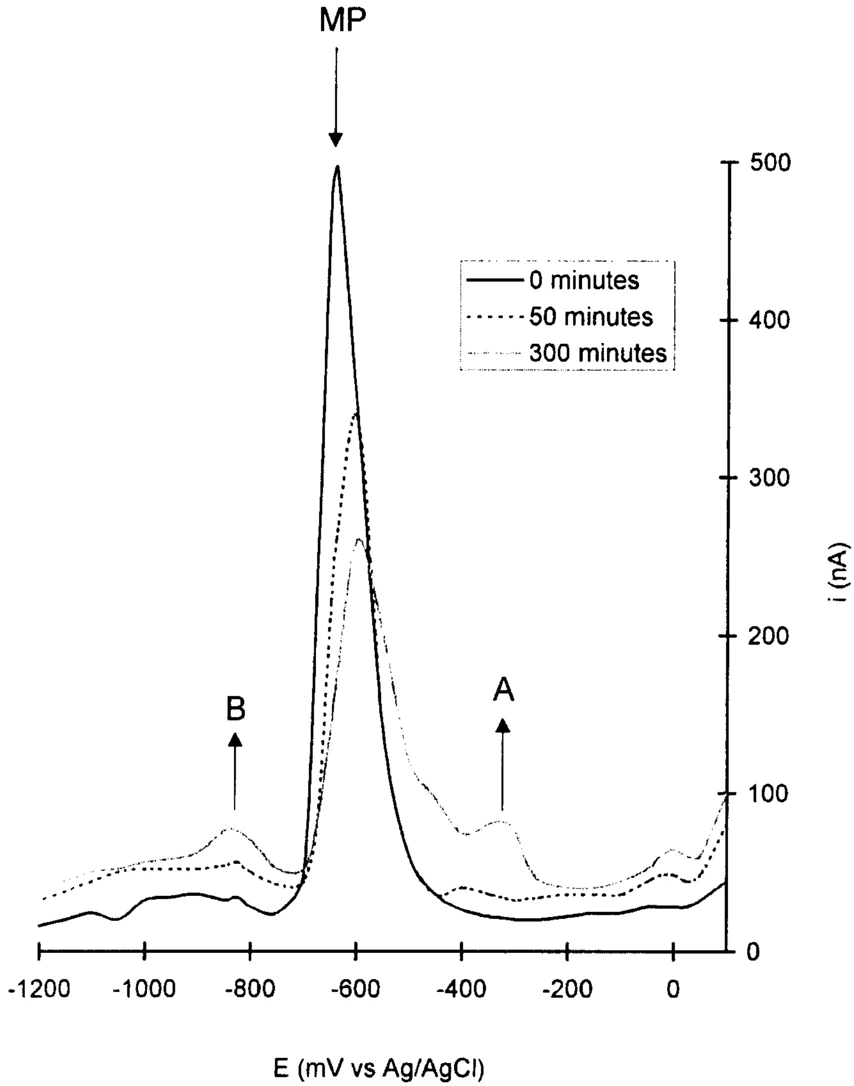


FIGURE 2 Polarograms of methylparathion (MP) recorded during its UV irradiation under oxygen atmosphere. [MP] = 5×10^{-5} mol dm^{-3}, $\lambda = 254$ nm

b) In the presence of metallic mercury

Because metallic mercury absorbs ultraviolet light (254 nm), potentially afecting methylparathion degradation, the pesticide was next irradiated in the presence of metallic mercury. Experimental results show in this case that more irradiation time was required for a quantitative conversion of methylparathion. Half life time was 325 minutes compared to 220 minutes in the absence of the mercury. Clearly mercury retards methylparathion photodegradation. Figure 3 provides some of the polarograms registered during the UV irradiation of methylparathion in the presence of metallic mercury.

c) In the presence of TiO_2

800 mg of TiO_2 were mixed with 25 mL of a 5×10^{-5} mol dm^{-3} methylparathion solution in 0.1 mol dm^{-3} lithium perchlorate, and the resulting whitish suspension was irradiated at 366 nm. Electroactive products were detected; with the signal of compound A becoming more intense than that of signal B. Figure 4 provides polarograms registered during the photolysis of methylparathion in the presence of TiO_2. The same experiment performed in the absence of TiO_2 produced no changes in the polarograms, making it clear that TiO_2 is working as a photosensitizer at this wavelength, a behavior that has recently been described for the photolysis of organic compounds[18–20].

In Figure 5 graph shows ip versus time of disappearance of methylparathion under different experimental conditions.

Estimated values of the rate constant (k) and their corresponding half life times under different experimental conditions are shown in Table I. The methylparathion degradation followed a kinetics of a pseudofirst order since the amount of added reagent was always greater than the initial quantity of the pesticide. Similar degradation times were observed, except when the metallic mercury was present during the irradiation. Half life times hardly differed when the photodegradation was carried out directly on the methylparathion (254 nm) or indirectly, with TiO_2 interceding (366 nm).

Photodegradation products

The photodegradation products were extracted with a (10:1) water-chloroform mixture, and IR and GC-MS analysis were carried out. Analysis of the IR spectrum of the compound A established the following: The $-NO_2$ group did not transform and the related bands were not modified (streching asymmetric $C-NO_2$ 1570–1500 cm^{-1}; streching symmetrical $C-NO_2$ 1370–1300 cm^{-1}). Bands around 2850–2050 cm^{-1} (which are related to the vibrations of C-H), appeared more intense in the IR spectrum of the product in comparison to those of the methylparathion. A broadband (3417 cm^{-1}), characteristic of OH groups, and a medium intensity band at 1727 cm^{-1} characteristic of carboxylate groups were also observed. These were not initially present in the IR spectrum of the methylparathion. A comparison of these bands with literature data[21–22] established

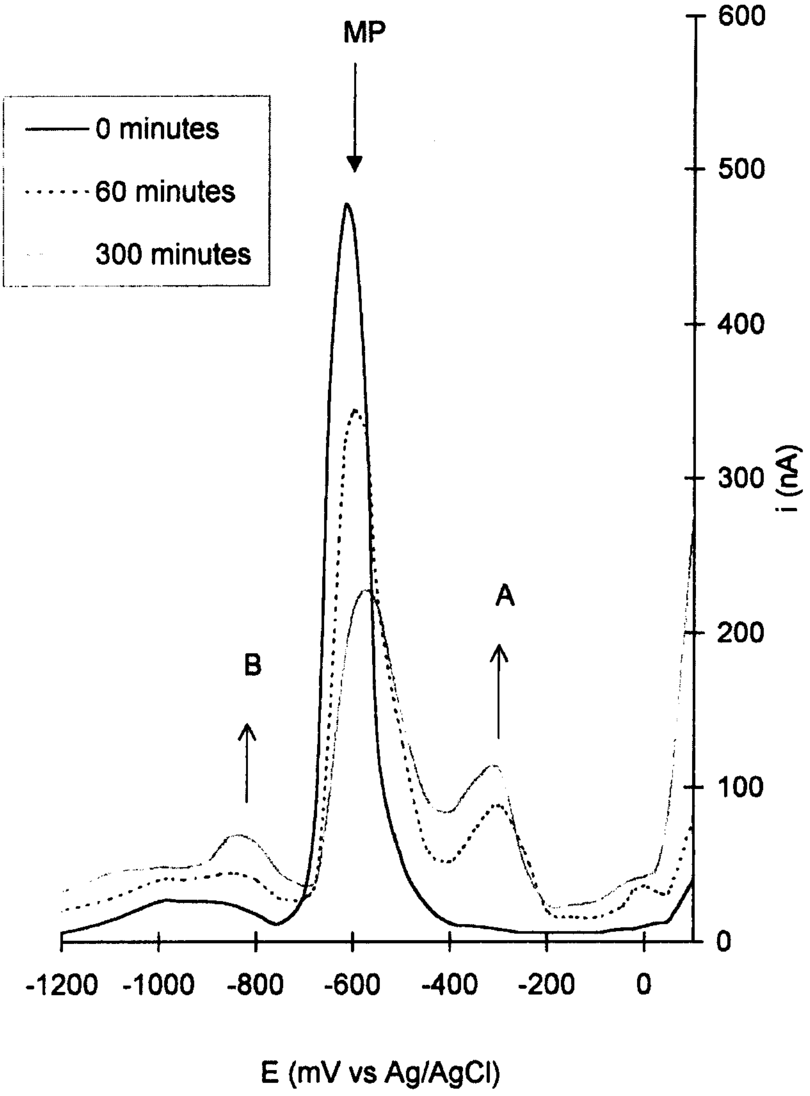


FIGURE 3 Polarograms of methylparathion (MP) recorded during its UV irradiation in the presence of metallic mercury under oxygen atmosphere. [MP] = 5×10^{-5} mol dm^{-3}, $\lambda = 254$ nm

that a carboxylic group exists in compound A. GC-MS analysis certified the existence of residual methylparathion, and also detected a compound with a molecular weight of 167 that likely corresponds to p-nitrobenzoic acid (PNBA). To support spectroscopic data, a PNBA standard was added to the irradiated

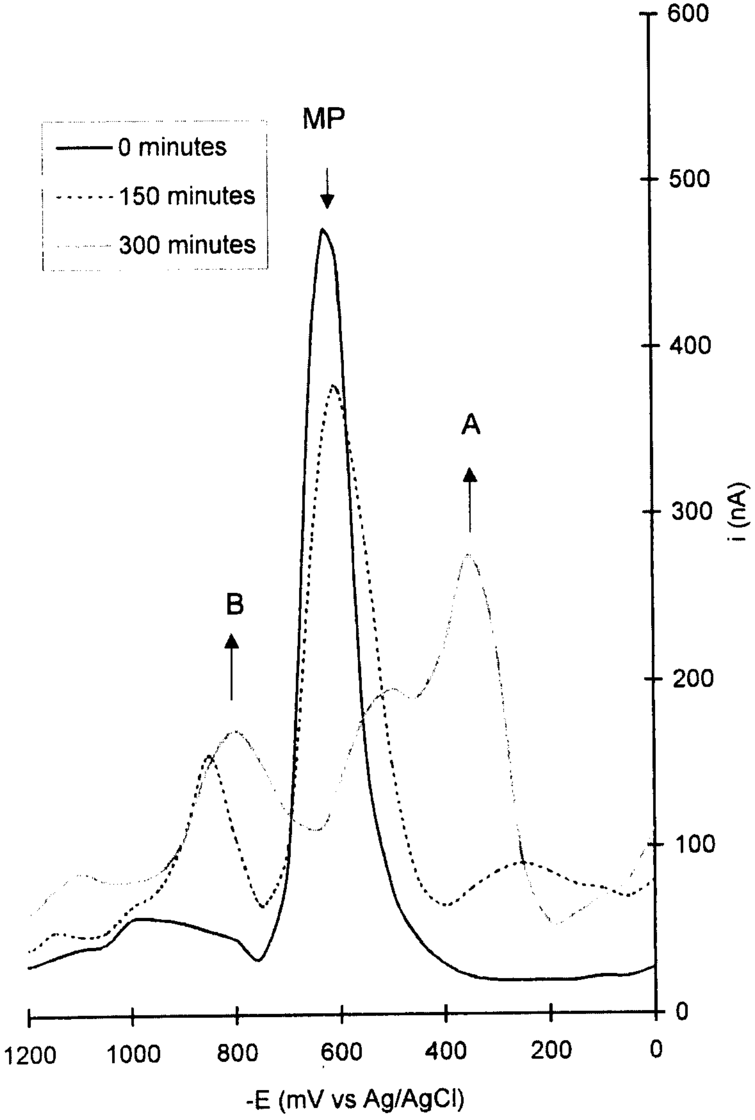


FIGURE 4 Polarograms of methylparathion (MP) recorded during its UV irradiation in the presence of TiO_2 under oxygen atmosphere. [MP] = 5×10^{-5} mol dm^{-3}, λ = 366 nm

solutions in order to confirm its presence. PNBA showed a polarographic signal identical to the signal of compound A (Ep = –0.34 V). Spectroscopic and electrochemical data support the conclusion that compound A is PNBA.

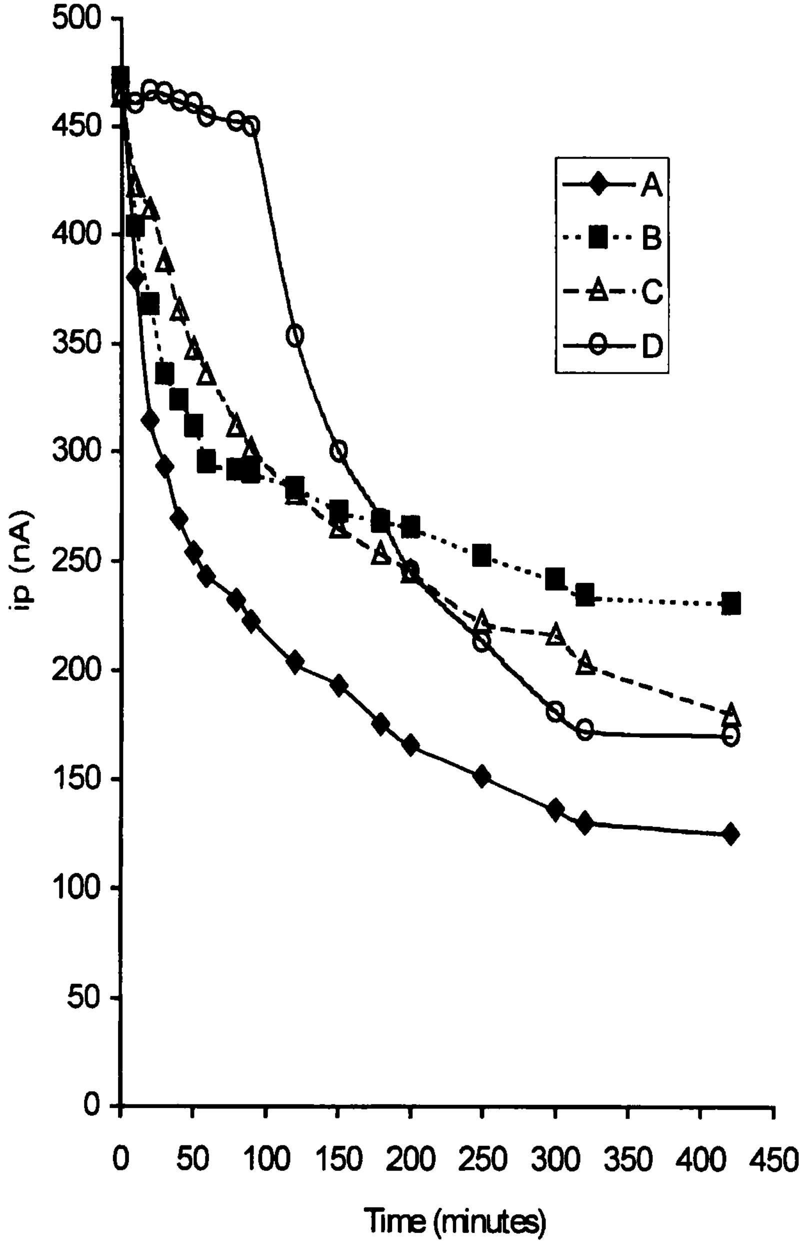


FIGURE 5 Graph of ip vs. time of disappearance of methylparathion under different experimental conditions. [MP] = 5 × 10^{-5} mol dm^{-3}. A: under nitrogen atmosphere; B: under oxygen atmosphere; C: in the presence of metallic mercury and D: in the presence of TiO_2. A, B, and C at 254 nm and D at 366 nm

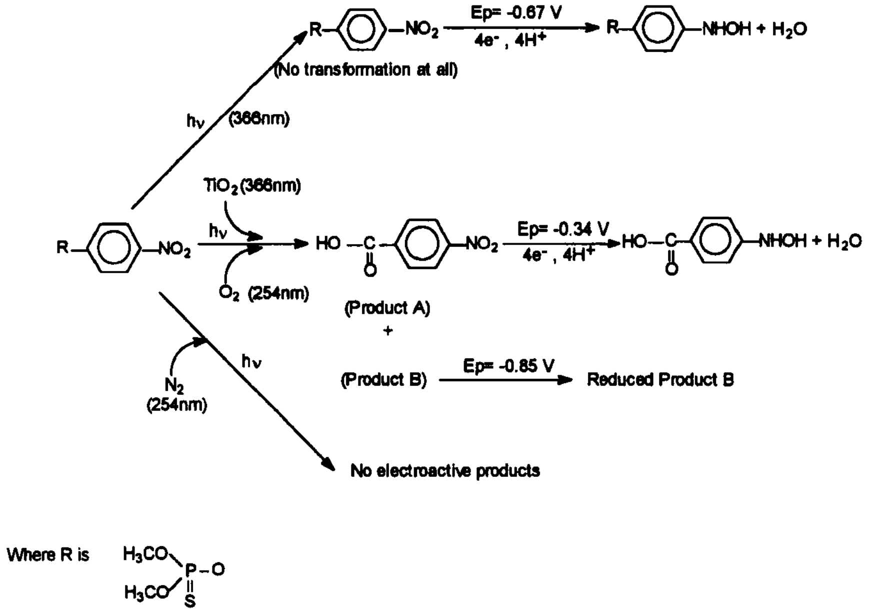
TABLE I Values of the reaction rate constant (k) and half life times for the degradation of methylparathion in an aqueous medium (0.1 mol dm^{-3} $LiClO_4$, pH 6.5) by UV irradiation

Experimental conditions	*Half life time (min)*	$k \times 10^5$ (s^{-1})
Nitrogen atmosphere; $\lambda = 254$ nm	203	5.69
Oxygen atmosphere; $\lambda = 254$ nm	220	5.25
Metallic mercury under oxygen atmosphere; $\lambda = 254$ nm	325	3.55
TiO_2 under oxygen atmosphere; $\lambda = 366$ nm	215	5.36

In the IR spectrum of the compound B was observed the permanence of the bands associated with the -NO_2 group, which suggests that this functional group did not transform during photolysis. Bands around 2850–2050 cm^{-1}, characteristic of vibrations of C-H, and a broadband around 3650–3150 cm^{-1}, that was associated to the group OH, were also observed. GC-MS analysis only showed the existence of residual methylparathion. On the other hand, the polarographic reduction peak of compound B (Ep = –0.85 V) is close to the reduction peak of p-nitrophenol (Ep = –0.93 V), that excludes the existence of p-nitrophenol, possibly presenting a similar structure. Consequently, there is not enough experimental evidence that could verify the chemical structure of the compound B.

The general mechanism of photoassisted transformation does not depend on the experimental conditions, as the main products were similar under the different conditions. The sequence of reactions, based on the experimental results, is shown in scheme 1.

In this scheme methylparathion degradation was not observed when the pesticide was irradiated at 366 nm, thus its polarographic signal did not change (reduction peak at –0.67 V remained). When the pesticide was irradiated at 254 nm under N_2 atmosphere no electroactive products were detected, although the reduction peak of the methylparathion diminished, indicating its degradation. On the other hand, both irradiation under O_2 atmosphere (254 nm) and in the presence of TiO_2 (366 nm) yielded two electroactive products, compound B (Ep = –0.85 V) and compound A (Ep = –0.34 V), identified as PNBA, the predominant product in all experimental conditions. The PNBA carboxyl group is probably formed by a mechanism of free radicals given the condition of the reaction (scheme 2). Its also possible that as an initial step, a homolytic cleavage between the oxygen of the dimethylthiophosphate group and the nitrophenyl takes place over the TiO_2 and the dimethylthiophosphate group keeps degrading producing methyl radicals and forming as a final product thiophosphoric acid[23–25]. Subsequently, the methyl radicals react with the nitrophenyl radical forming p-nitrotoluene. In the reaction medium, hydrogen peroxide can be formed as a

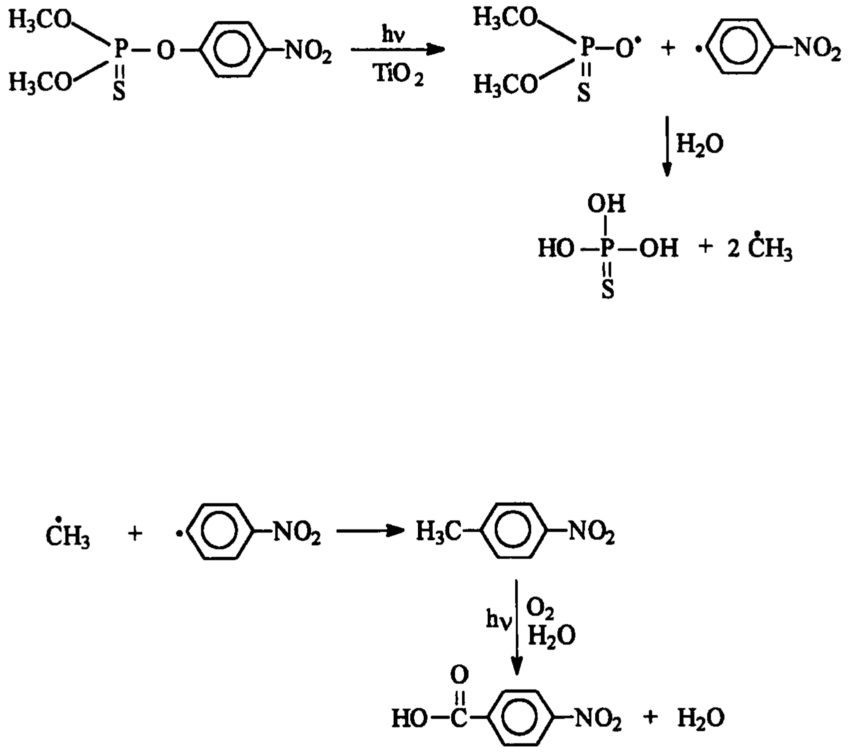


SCHEME 1 Electroactive products of methylparathion UV irradiation in an aqueous solution (0.1 mol dm^{-3} $LiClO_4$, pH 6.5)

product of the photochemical reaction between water and oxygen, which in its turn will decompose in oxhydrile radicals[26]. The methyl group of the p-nitrotoluene can be oxidized by the oxhydrile radicals or with oxygenated water producing PNBA[27].

CONCLUSIONS

When methylparathion was irradiated at 254 nm, transformation of the pesticide varied depending on the experimental conditions. Degradation of the pesticide was not observed after several hours of irradiation at 366 nm; however, when TiO_2 was added to the methylparathion solution and it was irradiated at 366 nm, the pesticide underwent complete transformation, thus demonstrating the TiO_2 photosensitizer effect. Two electroactive products (A and B) were observed; these presented reduction peak potentials at –0.34 and – 0.85 V, respectively. Compound A was the majority product. Spectroscopic and electrochemical data support the conclusion that compound A is p-nitrobenzoic acid. Reaction rate constants for the photolysis of methylparathion ranged from 3.55×10^{-5} to



SCHEME 2 Possible phototransformation route of methylparathion to obtain p-nitrobenzoic acid

5.69×10^{-5} s^{-1}, and their corresponding half life times ranged from 325 to 202 minutes. This indicates that outside of the experimental conditions in which the photolysis took place, the processes occurred at similar rates, except in the presence of metallic mercury, and they presented a kinetic of pseudofirst order, following the disappearance of the methylparathion.

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