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Photodegradation of Parathion

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Parathion (O,O-diethyl O-p-nitrophenyl thiophosphate) is one of the most common organophosphorus pesticides used in agriculture. Field studies have shown that the lifetime of sprayed parathion is very short, largely because of photochemical reactions initiated by absorption of sunlight in the ultraviolet region (Moilanen et al. 1975; Woodrow et al. 1978). Because of its high toxicity, possible environmental contamination due to the application of parathion has been a public and governmental concern (Crosby, 1984). The problem is aggravated by the findings that the products of its photochemical reactions may also be toxic. For example, parathion and one of its photochemical products, paraoxon, have been shown to be inhibitors of cholinesterase (Arterberry et al. 1961; Kimura, 1963). Another product, O,O,S-triethyl thiophosphate, belongs to a class of compounds which have been reported to show delayed toxic effects and limited anticholinesterase activities (Gazzard et al. 1974; Ali et al. 1982). The synergistic toxicity between parathion and the triethyl thiophosphate has also been implicated (Grunwell et al. 1973).

The photochemistry of parathion has been studied by several groups of investigators (Grunwell et al. 1973; Mansour et al. 1983; Meallier et al. 1977; Moilanen et al. 1975). However the results of the various groups differ significantly both in the type and number of products observed. For example, in the liquid phase studies Grunwell et al. (1973) identified six products with O,O,S-triethyl thiophosphate and triethyl phosphate as the main species, and paraoxon as a minor product; while Mansour et al. (1983) reported paraoxon and p-nitrophenol as the major products. The main reason for such discrepancies could be the differences in reaction conditions. For systems in which secondary processes are involved, it is expected that factors such as duration of irradiation and intensity of light would be important in determining the distribution of products. In the present study an attempt has been made to differentiate products into those which are formed in the initial stage and those which are formed in the

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secondary processes in the photolysis. It is hoped that this would lead to a better understanding of the photoreactions of parathion and thus shed light on the environmental problems associated with the use of the pesticide.

MATERIALS AND METHODS

Parathion and paraoxon (both of purity $>$ 99.9%) were obtained from the Riedl-de-Haen Company and were used without further purification. Triethyl phosphate was purchased from Aldrich chemicals. p-Nitrophenol was obtained from Merck. 0,0-Diethyl 0-phenyl thiophosphate was prepared by modifying the method for parathion synthesis (Fletcher et al. 1948). 0,0,S-Triethyl thiophosphate,to be used as a GC and GCMS standard, was prepared by the method of Bracha et al. (1968), characterization of the thiophosphate as a photolysis product was not affected by small amount of impurities which may have been present (Gazzard et al. 1974). Analytical grade methanol obtained from BDH chemicals was used as solvent without further treatment.

Gas chromatography was performed on a Hewlett Packard chromatograph model 5790A, equipped with a flame ionization detector and a Chrompack CP-Sil 5 fused silica capillary column, 25 m in length and 0.23 mm inside diameter. Combined gas chromatography-mass spectrometry was carried out on either a VG Micromass model 7035 instrument with a Hewlett Packard model 5710A GC or on a Hewlett Packard mass selective detector, model 5970, with a model 5790A GC.

Irradiation of solutions involved the use of a high pressure, short arc xenon lamp from Varian, model VIX-150, or a medium pressure mercury lamp from Hanovia, type SH 616, which was of lower output than the xenon lamp. A combination of two Corning filters CS 9-54 and CS 0-53 effectively cut off light of wavelength shorter than 280 nm, and a high intensity grating monochromator (Baush & Lomb model 33-86-75) was used when monochromatic light was needed. Most of the irradiation was performed using rectangular quartz cells of 2 mm pathlength. An RCA 935 phototube was used to monitor the constancy of light intensity during photolysis.

Photolysis was conducted on solutions of parathion in methanol with concentrations in the millimolar range. Each solution also contained the hydrocarbon contane, C_{20}, with concentration equal to a fraction ca 10% of that of parathion, as internal standard for GC analysis. The hydrocarbon was checked to be inert toward the radiation used for photolysis. In a typical experiment, a solution in a photolysis cell was irradiated for the required period. GC analysis of the solution was carried out immediately after irradiation by direct injection of 2 uL aliquots using the splitless injection method; the column temperature was held at

Table 1. Product formation during photolysis of parathion in methanol*; initial concentration = 2.29×10^{-3} M

Time of irradiation (min)	% parathion decomposition	Products observed
5	6.0	1,2,7**
10	9.4	1,2,3,7
20	17.1	1,2,3,4,5,6,7
40	27.9	1,2,3,4,5,6,7

* Light source: mercury lamp-Corning filters
** Component 7 was an unidentified product

100°C at injection, then programmed to 250°C at 10°C min^{-1}. No preconcentration of solution was required.

For photolysis under degassed condition, a degassing apparatus was used. The apparatus consisted of a round flask connected through a side arm to a cylindrical cell of 1 cm pathlength. A solution in the flask was degassed by a few freeze-evacuate-thaw cycles on a vacuum line, the degassed solution was then transferred to the cell and irradiated.

RESULTS AND DISCUSSION

The absorption spectrum of parathion in methanol showed a strong but structureless band extending from 240 to 350 nm with the band maximum situated at 273 nm and with a ϵ_{max} value of 1.30×10^4 $M^{-1} cm^{-1}$. The intensity and position of the band suggests that it is due to the $\pi - \pi^*$ transition of the aromatic ring (Friedel and Orchin, 1951).

The radiation emerging from the xenon lamp-Corning filter combination showed a steep rise in intensity from 280 nm and reaching a shoulder near 400 nm, closely resembling the ultraviolet portion of the spectrum of terrestrial solar radiation (Thekaekara et al. 1971). On the other hand, the radiation obtained from the mercury lamp-Corning filter combination showed intensity maxima at 365, 313, 302 and 297 nm in the ultraviolet region. The two lamps differed greatly in intensity but did not give significant differences in product distribution when they were used for irradiation of parathion.

Irradiation led to gradual decrease of parathion concentration and formation of products with GC retention times generally shorter than that of parathion. The following products were found:

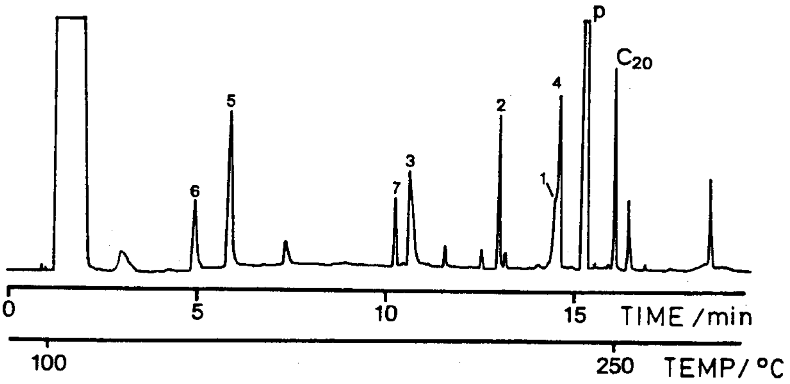
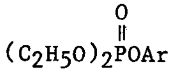
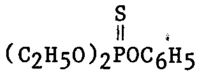


Figure 1. Chromatographic trace of parathion solution after potolysis. p = parathion


$(C_2H_5O)_2\overset{\overset{O}{\|}}{P}OAr$

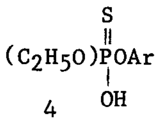
1


$(C_2H_5O)_2\overset{\overset{S}{\|}}{P}OC_6H_5$

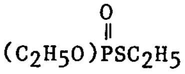
2

HOAr

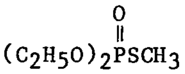
3


$(C_2H_5O)\underset{\underset{OH}{|}}{\overset{\overset{S}{\|}}{P}}OAr$

4

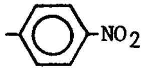

$(C_2H_5O)\overset{\overset{O}{\|}}{P}SC_2H_5$

5


$(C_2H_5O)_2\overset{\overset{O}{\|}}{P}SCH_3$

6

Ar =



These products, except 4 and 6, were identified with the aid of authentic compounds. The identifications of 4 and 6 were based on the analysis of their mass spectra and GC retention times. The number of products observed increased with the extent of photolysis as illustrated in Table 1. Upon more extensive photolysis, triethyl phosphate was also detected as a product. Extensive photolysis also led to formation of other minor product components as well as components with retention time longer than that of parathion. A typical GC trace which corresponds to an extensively irradiated sample is shown in Figure 1.

During photolysis the concentration of product 1, paraoxon, initially increased linearly with time; upon longer irradiation, the concentration of 1 decreased and then remained at a low level. This pattern of change can be explained by the occurrence of photoreactions of 1 itself. Separate photolysis of 1 under comparable conditions showed similar rate of photoreaction as parathion. This is illustrated in Figure 2. When 1 was photolysed to about twenty percent conversion, the chromatogram

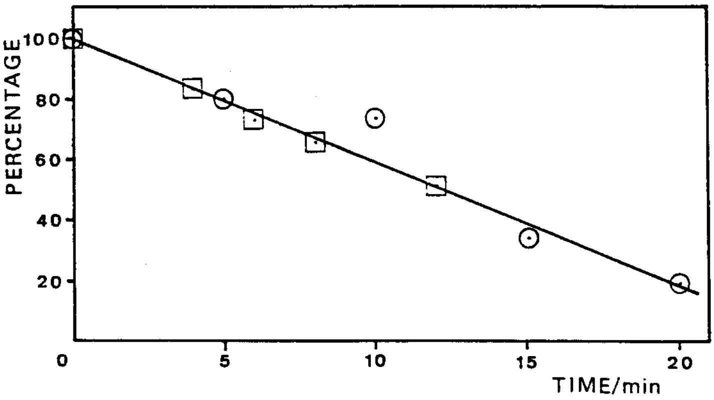


Figure 2. Percentage of undissociated compound vs time of irradiation. Circles: parathion; squares: paraoxon. Light source: xenon lamp-Corning filters.

showed six products, these included p-nitrophenol, triethyl phosphate and four unidentified components.

Compound 2, 0,0-diethyl 0-phenyl thiophosphate has not been reported previously, although it is a major product observed in the present work. Figure 3 shows that the increase of GC peak area with time is approximately linear (up to about 28% of parathion disappearance). The formation of this compound apparently involved the unimolecular cleavage of carbon-nitrogen bond in the aromatic moiety, a mode of reaction which has been reported as a major process in the photolysis of aromatic nitro compounds (Calvert and Pitts, 1962).

Compound 4, 0-ethyl 0-p-nitrophenyl thiophosphate, has a GC retention time very close to that of 1, leading to partial overlap of the two peaks even on the high resolution capillary column. Clearly, previous studies with packed columns might assume the peak to be due to only compound 1, leading to erroneous conclusions. The compound was detected only after appreciable decomposition of parathion had taken place, however its peak height eventually surpassed that of 1 upon further photolysis. Interestingly compound 4 was previously proposed as a possible product by Meallier et al. (1977).

Under degassed condition, the rate of disappearance of parathion was found to be appreciably greater than that in aerated solution. However the same products were observed and their relative concentrations were also similar to those observed for aerated solution. This indicates partial quenching of the photo-reactions by dissolved oxygen and thus at least part of the reactions may originate from a low-lying triplet excited state.

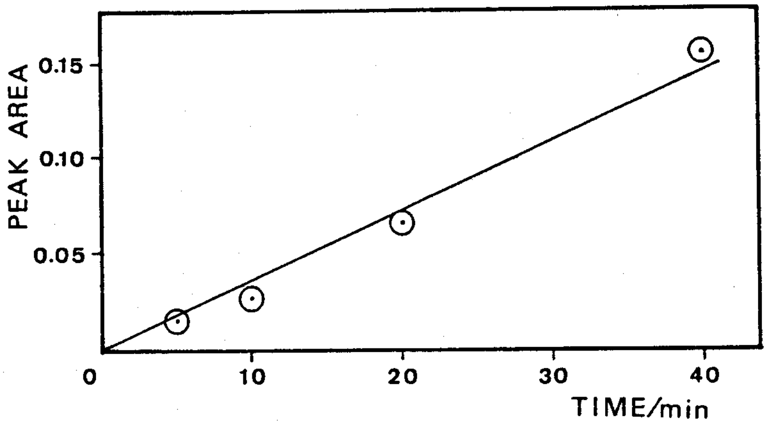


Figure 3. Peak area (relative to C_{20}) of 0,0-diethyl 0-phenyl thiophosphate vs time of irradiation.
Light source: mercury lamp-Corning filters.

Notably the relative yield of paraoxon formed under degassed condition was comparable to that in aerated solution, thus it is unlikely that the formation of paraoxon involved reactions with molecular oxygen. For aerated solution, the quantum yield of parathion disappearance at 254 nm was found to be $6x10^{-4}$, and the quantum yields of formation of 0,0-diethyl 0-phenyl thiophosphate and p-nitrophenol were approximately one order of magnitude lower.

The linear increase in concentration with time during the initial period of photolysis, observed for compounds 1 and 2, suggests that these compounds were formed in the primary process of excited parathion. In contrast, compounds 3, 5 and 6 were not observed in the initial stage, but only appeared after appreciable decomposition of parathion had occurred. These compounds were thus likely to be products of secondary processes. The formation of triethyl phosphate after prolonged photolysis can be attributed at least partly to subsequent photo-reactions of paraoxon.

When ethanol was used to replace methanol as solvent, irradiation of parathion led to the formation the products 1-5, but product 6 was not detected, suggesting that the formation of 6 may involve reactions with the solvent methanol. Component 6 was formed only after appreciable decomposition of parathion had taken place and its yield was generally small compared to the other products.

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