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Action of Sunlight on Parathion

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Parathion is one of the most important organophosphorus insecticides and is used extensively in agriculture as a contact insecticide. Its toxicity is very high, and its physicochemical behavior in the atmosphere, in water, and in the soil make it an environmental chemical which produces manifold biological and ecological effects.

Despite the highly specific action of this substance based on its suitability as a contact insecticide and stomach poison, any general toxicity extending beyond its area of application is a latent danger for the neighboring biosphere. Since the initial use, enduring attention has therefore been devoted to its stability to the weather and other influences, to the resulting chemical transformations, and to the nature of the important chemical and biological properties of transformation and decomposition products.

While both parathion and paraoxon, on the one hand, have an excellent insecticidal action, they are also toxic to warm-blooded animals. Paraoxon is water-soluble and can penetrate into plants and there develop a systemic insecticidal action.

The photochemical behavior of parathion in sunlight has been little studied. Photochemical oxidation with different wavelengths ($\lambda < 300$ nm) led to a variety of light intensity and wavelength dependent photoproducts. Biological degradation, to the extent it has been investigated (LICHTENSTEIN et al. 1972, ZUCHERMANN et al. 1970), has shown the formation of 4-nitrophenol, 4-aminophenol, and paraoxon. Biological transformation in the soil led to the formation of paraoxon, 4-nitrophenol, and O,O-diethyl phosphate. The toxicity accumulates in the soil and in sediments by virtue of adsorption and desorption phenomena.

In addition to biological degradation and hydrolytic processes, photochemical reactions can play an important role in the breakdown of parathion in aqueous medium. In rivers and aquatic media the organophosphorus pesticides undergo various transformations. Under natural conditions photochemical transformation reactions in the presence of sunlight are especially important when the different environmental factors are considered.

Parathion can persist for long periods in dry soil and may be converted to the highly toxic paraoxon and related products (SPENCER et al. 1975). Paraoxon is formed in solution when ozone acts on parathion (GUNTHER et al. 1970) and with UV light (GRÜNWELL & ERICKSON 1973). SPENCER et al. 1978 reported that under atmospheric conditions oxidation especially influences the transformation rates of parathion to paraoxon.

MATERIALS AND METHODS

In order to establish the photochemical reactivity, parathion was irradiated with a Hg low-pressure lamp in water, methanol, 2-propanol, and various aqueous solvent mixtures. To improve mixing a current of nitrogen was blown through the experimental reaction mixture; the decrease was followed by gas chromatography. A Philips HPK 125 lamp yielding 17 x 10^{-3} mol quanta per hour and enveloped in a Pyrex glass cooling jacket was used. About 95% of the lamp dipped into the reaction mixture cooled to 20 - 25° C. The identity of the compounds obtained was confirmed gas-chromatographically by a comparison with authentic substances.

Laboratory Experiments. 10 mg parathion were dissolved in 1 L distilled water. 100 mL portions of this solution were irradiated for 2, 5 and 10 h in an irradiation vessel with $\lambda > 290$ nm. Afterward, the solutions were extracted with 3 x 50 mL chloroform, which was removed to dryness under mild conditions (rotary evaporator; vacuum, 11 Torr; bath temperature 27 - 30° C). The residue was taken into 1 mL acetone. The samples were stored in brown glass vials until analyzed. TiO_2, ZnO, MgO were used without further treatment. Each photolysis 500 mg in a mixture of distilled water (100 mL) and organic substance (5.7 x 10^{-4} mol/L) was irradiated with $\lambda > 290$ nm. The solution was stirred by a magnetic stirrer. After photolysis, the solution was acidified with HCl, then extracted with diethylether, which was finally concentrated under reduced pressure. The photoproducts were determined by gas chromatography.

Chemicals. All solvents were of analytical reagent quality and were obtained from E. Merck, D-6100 Darmstadt, FRG. Hydrogen peroxide (30%) was obtained from Fluka, D-7910 Neu-Ulm, FRG. Parathion ethyl and paraoxon, both from Riedl-de-Haen, D-3016 Seelze, FRG, were of the highest available purity ($>$99%). The

Table 1. Photolyses of Parathion Solutions

(nm)	Solvent	Aerated or Degassed	Photolyses Times (h)	Degradation of Parathion (%)	Products (%)	
					Nitrophenol	Paraoxon
290	H_2O	Aerated	2	19	1.5	2
			5	80	4	0.5
			10	88	8	-
290	MeOH	Degassed	10	21	5.4	Trace,1.8
290	$(H_2O/MeOH)$ [a]	Aerated	10	14	8	Trace,0.5
290	$(2\text{-}PrOH/H_2O)$ [b]	Degassed	10	9	2	Trace,1.3
290	$(H_2O/MeOH/H_2O_2)$ [c]	Degassed	2	20	Traces	-
290	(H_2O/H_2O_2) [d]	Degassed	2	73	10	-
290	H_2O/ZnO	Aerated	1	29.8	2.5	-
	H_2O/MgO	Aerated	1	35	1	-
290	H_2O/CdS	Aerated	1	41	3	-
290	H_2O/TiO_2 [c]	Aerated	1	16	5	-

a) water/methanol (60/40 by vol.)
b) 2-propanol/water (70/30 by vol.)
c) water/methanol/hydrogen peroxide (≈ 30%), (500 mL/50 mL/0.01 mL)
d) water/hydrogen peroxide (≈ 30%), (0.001 mL/10 mL)

4-nitrophenol was >> 99% pure. TiO_2 (99%), ZnO (99%) and MgO (97%) were obtained from E. Merck.

Preparation of parathion standards. Parathion standards were prepared by dissolving the substance in 20 mL methanol and mixing well to give concentrations of 0.05 and 0.02 mg/mL. A standard curve was obtained by analyzing the solutions.

GC/MS analysis. Combined gas chromatography/mass spectrometry (GC/MS) was performed on LKB 9000 S, equipped with flame ionisation detector, 2 m x 2.5 mm glass column with 3% OV-17 on Gas-Chrom Q 80 - 100 mesh. The column was temperature programmed from 80 to 220° C at 6° C/min.; the carrier gas was helium.

Gas chromatography. A gas chromatography Carlo Erba Fractovap 2450 equipped with a flame ionisation detector and coupled to 1 mv recorder Linseis L 6501 with an electronic integrator Hewlett Packard 3881 A was employed. The analytical glass columns, 2 m x 3 mm ID were packed 1) 3% OV-17 on 80/100 mesh Gas-Chrom Q and 2) 1% SP 1240 deactivated for acidic compounds on 100/120 Supelcoport. The column temperature was programmed from 80 to 220° C at 6° C/min., with flame ionisation detector at 250° C. Nitrogen carrier gas flow was 40 mL/min.

RESULTS AND DISCUSSION

An investigation of the UV spectra in aqueous solution showed that λ_{max} lies at between 219 and 278 nm independently of pH. The molar extinction coefficients are at around 3900 for the first band and about 2900 for the second band (Fig. 1). A weak band at 390 nm of slight intensity is due to activation of the vibration states of the molecules or ionic dissociation in aqueous media. In addition to the solvent water, certain paramagnetic substances, for instance oxygen and certain organic main ingredients such as humic acids or lignin substances as sensitizers, may be expected to influence the kinetics of the photochemical decomposition in aqueous medium. In apolar solvents the results showed that the molecule is little polarized, but with increasing solvent polarity this property becomes enhanced. The rate of photodegradation depends on the solvent used and the increasing polarization of the molecule in the medium. This polarization leads to a loosening of the $\geq P - \bar{O}$ bond and makes possible the rate-determining proton addition step accompanied by splitting off of $(C_2H_5O)_2 \geq P = \underline{\overline{S}}$ and the formation of the basic p-nitrophenol and other photoproducts (Fig. 2). The experiments showed that the reaction proceeds more slowly in apolar solvents such as n-hexane and cyclohexane, while the

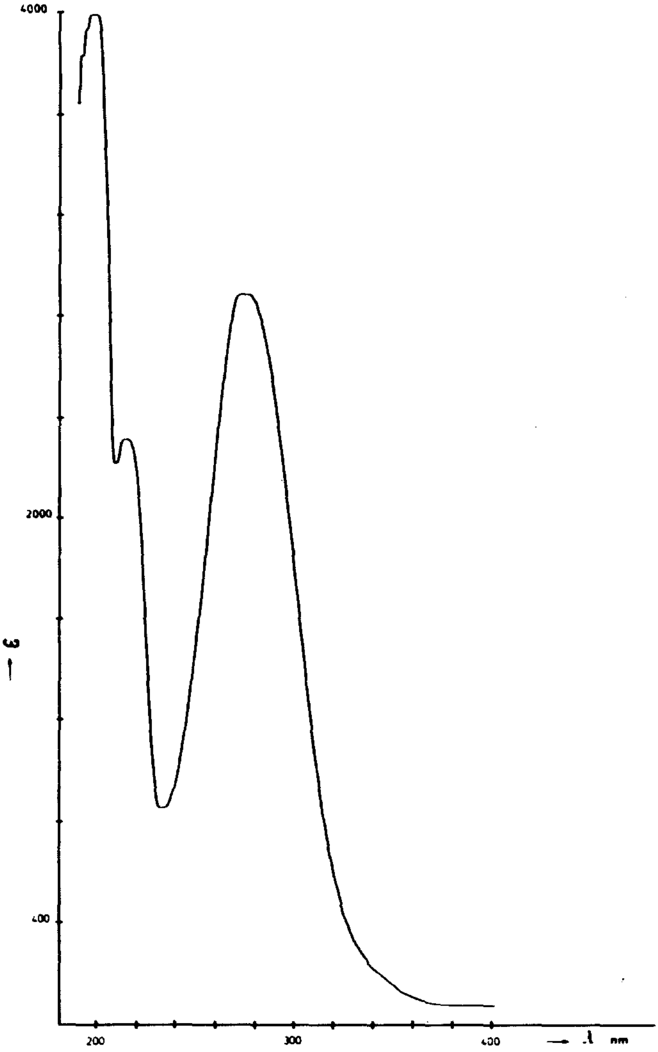

Figure 1. Ultraviolet absorption spectra of parathion in water

absence of an additional solvent produced its effect. In evaluating the results a fundamental distinction can be made between two principal reactions involved in the photochemical decomposition of parathion. (a) a free-radical mechanism in apolar solvents, and, (b) an ionic breakdown in aqueous solvents.

The photoproducts,too,decompose at a relatively high rate in the presence of oxygen. Our investigations of the direct photolysis of parathion did not embrace all details, but they showed that the decomposition at wavelengths greater than 290 nm in water at pH 6.4 proceeds very slowly. The quantum yield was found to be 1.5×10^{-3}.

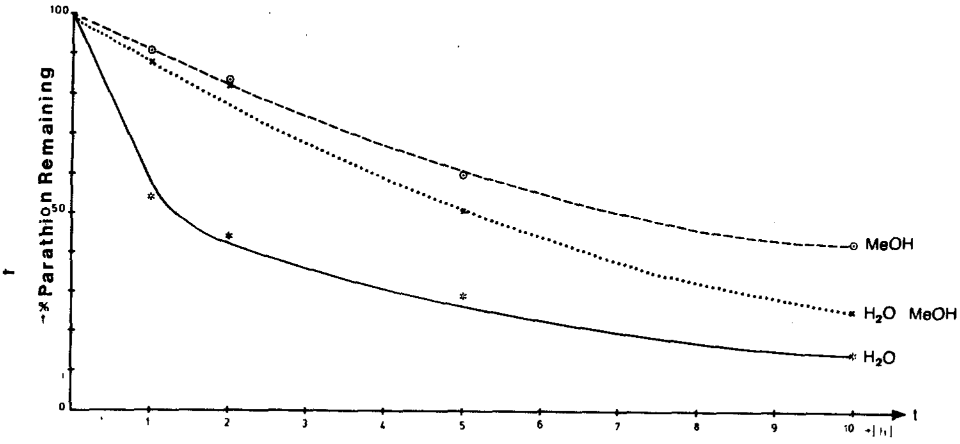

Figure 2. Parathion photodegradation rate at 26° C and pH 6.5
Initial concentration was 3.43×10^{-5} mol/L

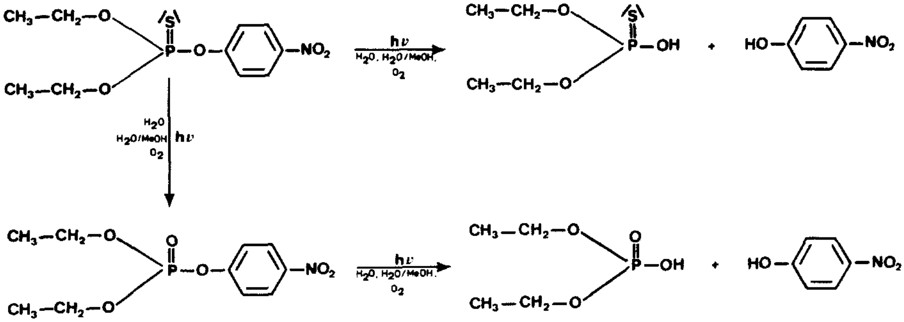

Figure 3. Photooxydation pathways of parathion

The half-life of the hydrolytic breakdown of parathion was determined and found to be 65 h in the water of the river Isar at pH 7.8. Irradiation of 5×10^{-2} mol/L p-nitrophenol showed that after 20 h 25% was broken down in methanol and 31% in ethanol. On the other hand, the decrease in concentration in water proceeded faster. Dinitro- or trinitro-derivatives could not be identified. The half-lives of p-nitrophenol agreed relatively well with earlier results. Since p-nitrophenol is a weak acid, the half-lives depend strongly on the pH value of the solution. Free phenol is broken down the fastest, while the phenolate anion requires at least twice as long (HUSTERT et al. 1981). Photolysis of hydrogen peroxide can act as source of OH-radicals and can play a significant role in the oxidation of chemicals. Furthermore, OH-radicals react with different substance classes and thus have a special importance in the degradation of chemical compounds in different phases. The reaction rate with several oxides (TiO_2, MgO, ZnO) shows that the behaviour of the investigated substance toward an oxide depends on the polarity of the oxide. We hereby report that the relative amounts of the photoproducts were dependent on the reaction time.

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