

Photolysis Experiments on Phosmet, an Organophosphorus Insecticide

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The organophosphorus insecticide phosmet is used in plant protection as well as against parasites on animals. Phosmet showed numerous photoinduced reaction pathways, which first were studied in the presence of model environments for animal fur lipids (e.g., wool wax). The model solvents for saturated and unsaturated lipids were cyclohexane and cyclohexene, whereas methanol and 2-propanol were used as models for primary and secondary alcohol moieties of lipids. The measured degradation rates over an irradiation period of 7 h in all solvents used were very similar (49–55%). The obtained photoproducts generally included phthalimide, *N*-hydroxymethylphthalimide, and *N*-methoxymethylphthalimide. Furthermore, depending on the solvent used, additional degradation products were detectable as *N*-isopropoxy- and *N*-methylphthalimide in the presence of 2-propanol and cyclohexene, respectively. However, in the presence of cyclohexene, despite the similar turnover, distinctly lower concentrations of photoproducts were found, indicating further still unknown degradation pathways. Irradiations in methanol with increasing percentages of water led to higher degradation rates; however, the products were found to be the same. Irradiation experiments with pure phosmet on silica TLC plates and glass surfaces resulted in degradation rates of 19 and 32%, respectively, after 6 h. The results obtained clearly demonstrate for the first time that the photoinduced degradation of phosmet is strongly dependent on the chemical environment, affecting less the turnover than the photoproducts formed. The results additionally demonstrate the need to investigate the degradation behavior of phosmet on wool and in the presence of wool wax.

KEYWORDS: Phosmet; photodegradation; organophosphorus insecticide

INTRODUCTION

Phosmet [phosphorodithioic acid, *S*-[(1,3-dihydro-1,3-dioxo-2*H*-isoindol-2-yl)methyl] *O,O*-dimethyl ester, **1**, **Figure 1**] is a nonsystemic organophosphorus insecticide belonging to the subclass of dithiophosphates. It is commonly applied on plants (e.g., cotton, fruit, and potatoes) as well as on animals [e.g., cattle, pigs, sheep, and dogs (through dog collars)] in commercially available formulations such as Imidan, Prolate, or GX-118.

To the best of our knowledge, no studies on the photodegradation of pesticides on animals have been published yet, in particular not for phosmet. Some experiments on photodegradation rates of organophosphorus insecticides in wool have been undertaken, but no degradation products were identified (1). The same authors also mentioned from earlier studies that insecticides dissipated from sheep more rapidly during summer as compared to winter conditions, which was presumably attributed to sunlight and summer heat (2).

After application on animal skin or hair, phosmet is directly exposed to sunlight during the grazing of sheep or cows. Due

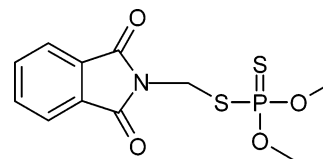


Figure 1. Structure of phosmet (1).

to the lipid environment of animal hair or sheep wool, pesticides can be photodegraded in a quite different manner as compared to that in an aqueous environment, also yielding degradation products different from metabolites usually found during *in vivo* or *in vitro* studies. Additionally, bimolecular reaction with lipids' constituents may result in photoaddition products so far unknown, which cannot be detected, for example, in wool wax, by standard analytical methods of residue analysis.

Only a few photodegradation experiments have been performed on phosmet to date. In 1974, Tanabe et al. (3) irradiated solutions of phosmet in diethyl ether. As main degradation products, they identified *N*-methylphthalimide and *N*-methoxymethylphthalimide among numerous unidentified products. Further on they focused on clarifying the photoproducts resulting from irradiation of the first photolysis product *N*-methylphthalimide. Vaintraub et al. (4) and Weintraub et al. (5) described photodegradation experiments on silica plates and on apples.

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The objective of our study is the determination of the photodegradation and reaction pathways of phosmet, depending on the respective environments in different model solvents simulating animal skin fat (e.g., wool wax). Like many former studies (6–10) demonstrated, the photochemistry of pesticides depends in the first instance on the functional chemistry of the environment. As wool grease is a constituent element (10–25% w/w) of the sheared greasy wool and is a complex mixture of polyesters and monoesters of high molecular weight, free fatty acids, and alcohols (11, 12), in the first step several simple models were utilized for UV irradiation experiments, resembling common structure moieties of wool wax. Therefore, cyclohexane and cyclohexene, which are also parts of the skeleton of sterols, were generally used as models for saturated and unsaturated constituents, respectively, of animal skin or hair lipids (e.g., sheep wool wax). Methanol and 2-propanol were models for primary and secondary alcohol groups as they occur in free fatty alcohols, hydroxy fatty acids, and sterols. These simple models, following models for plant cuticle lipids introduced by Schwack (7–10), have proved to be the best practical way to study possible reaction pathways and product formation, prior to moving on to the more complex natural system. In our previous studies (8) we additionally showed that the photoproducts, derived through these simple model experiments, could as well be found on plant surfaces, which also confirms the utilization of model systems in the first step. Furthermore, the resulting products can effectively be used as analytical standards (13) for later studies in natural environments.

MATERIALS AND METHODS

Materials. All solvents used were of analytical grade or distilled prior to use. Cyclohexene (Merck, Darmstadt, Germany) was distilled over 10% of P₂O₅ (Roth, Karlsruhe, Germany) before use.

Water was purified by a Milli-Q 185 plus water purification system (Millipore Corp., Bedford, MA).

N-Methylphthalimide (Sigma-Aldrich, Steinheim, Germany), *N*-hydroxymethylphthalimide, and phthalimide (Fluka, Deisenhofen, Germany) were obtained as standards in analytical quality. Silica gel, 63–200 μ m (Merck) was stirred with 10% of nitric acid (65%) for 30 min, washed until neutral, and dried for 15 h at 130 °C before use for column chromatography.

Phosmet was extracted from Imidan [52% Phosmet (w/w), Siegfried Agro, Zofingen, Switzerland) with acetone in a Soxhlet apparatus and, after evaporation under reduced pressure, recrystallized from methanol twice before use. Spectroscopic properties [MS (ESI⁺), *m/z* 318 ([M + H]⁺); ¹H NMR (DMSO) δ 3.67 (6H, d, CH₃), 4.96 (2H, d, CH₂), 7.95–7.86 (4H, m, Ar–H); ¹³C NMR (DMSO) δ 54.32 (d, CH₃), 39.05 (d, CH₂), 123.80, 131.55, 135.23 (s, Ar–C), 166.39 (s, C=O); IR (ATR) (cm^{−1}) 3481, 3025, 2995, 2949, 2867, 1780, 1719, 1612, 1463, 1452, 1406, 1376, 1304, 1279, 1188, 1082, 1072, 914, 831, 819, 797, 722, 692, 676] and melting point of the obtained colorless crystals corresponded to the expected structure and data given in refs 14 (melting point) and 15 (IR spectra). The purity of the recrystallized phosmet was determined by HPLC to be >99% (UV, 220 nm). The log $\epsilon_{221\text{nm}}$ (methanol) calculated (4.69) matched the determined log $\epsilon_{221\text{nm}}$ (methanol) of the commercial standard substance (Pestanal, Sigma-Aldrich).

Syntheses. *N*-Methoxymethylphthalimide was synthesized by employing a modified procedure according to ref 16 starting from *N*-hydroxymethylphthalimide and absolute methanol. *N*-Hydroxymethylphthalimide (1.5 mmol, 260 mg) was dissolved in 6 mL of absolute methanol, and the reaction was catalyzed by 0.3 mL of sulfuric acid (98%). After 15 h at 70 °C, the mixture was neutralized with sodium hydrogen carbonate and extracted twice with diethyl ether. After evaporation of the solvent under reduced pressure, the crystal needles were recrystallized from ethanol (yield = 73% of theory). Spectroscopic properties corresponded to the proposed structure [MS

(ESI⁺), *m/z* 192 ([M + H]⁺), 209 ([M + NH₄]⁺), 160 ([M – MeOH]⁺); ¹H NMR (DMSO) δ 3.27 (3H, s, CH₃), 4.92 (2H, s, CH₂), 7.94–7.86 (4H, m, Ar–H); ¹³C NMR (DMSO) δ 56.73 (s, CH₃), 68.66 (s, CH₂), 123.75, 131.64, 135.12 (s, Ar–C), 167.96 (s, C=O); IR (ATR) (cm^{−1}) 2998, 2959, 2932, 2843, 1774, 1709, 1605, 1481, 1467, 1448, 1436, 1412, 1344, 1325, 1287, 1229, 1186, 1162, 1083, 985, 960, 912, 889, 852, 798, 722, 711, 693] and to published data [mp = 121–122 °C (ethanol) (16), mp 120–121 °C (17)].

Phosmet-oxon was synthesized from isolated phosmet by use of bromine solution (methanol, 200 mM). A solution of phosmet (20 mM) in methanol (1.5 mL) was treated with 1.5 mL of bromine solution and agitated for 2 min in the closed vessel. The excess of bromine was reduced with an aqueous solution of ascorbic acid. The reaction mixture was treated with saturated saline and extracted twice with diethyl ether. Extracts of five reaction mixtures were combined, the solvent was evaporated under reduced pressure, and the residue was dissolved in methanol and subjected to preparative HPLC. Fractions were collected, methanol was evaporated, and residual water phase was lyophilized (yield = 35% of theory). Spectroscopic data of the obtained colorless crystals agreed with the proposed structure [MS (ESI⁺), *m/z* 302 ([M + H]⁺), 319 ([M + NH₄]⁺), 340 ([M + K]⁺); ¹H NMR (DMSO) δ 3.67 (6H, d, CH₃), 4.97 (2H, d, CH₂), 7.95–7.87 (4H, m, Ar–H); ¹³C NMR (DMSO) δ 36.89 (d, CH₃), 54.75 (d, CH₂), 123.62, 131.41, 135.04 (s, Ar–C), 166.23 (s, C=O); IR (ATR) (cm^{−1}) 3041, 2960, 1777, 1719, 1610, 1465, 1423, 1382, 1307, 1286, 1244, 1189, 1160, 1085, 1012, 922, 836, 770, 685; mp = 68 °C].

General Techniques. High-performance liquid chromatography (HPLC) analyses of phosmet and photolysis products were carried out on an HP1100 system consisting of an autosampler, a gradient pump, and a diode array detector (DAD) module (Hewlett-Packard, Waldbronn, Germany). For data acquisition and processing HP ChemStation software (rev. A.06.01) was used. DAD was performed at wavelengths of 220, 250, and 320 nm, each with spectral bandwidth (SBW) 8 nm, ref 500 nm (SBW 100 nm). Separation was performed at 25 °C with a reversed phase analytical column (5 μ m Eurospher 100-C₁₈, 250 \times 3 mm, Knauer, Berlin, Germany) including a precolumn (Eurospher 5 μ m C₁₈, 5 \times 3 mm, Knauer), using a gradient system consisting of 20 mM phosphate buffer (pH 4.0) and methanol (injection volume = 10 μ L, flow rate = 0.5 mL/min): 0/50, 1/80, 12/100, 20/100, 28/50, and 31/50 (minute/percent methanol).

Preparative HPLC was carried out on a system consisting of two pumps (Kronlab, Sinsheim, Germany), an A0293 variable-wavelength monitor (Knauer), a C-R3A integrator (Shimadzu, Duisburg, Germany), and a Kronlab HPLC column (guard column, 50 \times 20 mm; column, 250 \times 20 mm; Nucleosil RP 18, 7 μ m); a gradient system consisting of ammonium formate buffer (10 mM, pH 4.0) and methanol as eluents (flow rate = 20 mL/min), with gradient as above, was used. Pumps were controlled by Prepcon software.

High-performance liquid chromatography–mass spectrometry (LC-MS) analyses were performed on an HPLC system (HP1100 as described above), coupled to a VG platform II quadrupole mass spectrometer (Micromass, Manchester, U.K.) equipped with an electrospray interface (ESI). For data acquisition and processing, MassLynx 3.2 software was used. The same gradient system as in HPLC analysis was used except the mobile phase, which consisted of 10 mM ammonium formate buffer (pH 4.0) and methanol. All other parameters remained as mentioned before. MS parameters: ESI⁺; source temperature, 120 °C; capillary, 3.5 kV; HV lens, 0.5 kV; cone ramp, 20–60 V. For LC analysis, the MS was operated in full-scan mode (*m/z* 80–1200).

Ultraviolet (UV) spectra were measured with a Perkin-Elmer Lambda2 instrument (Überlingen, Germany) or an HP1100 DAD module, respectively.

¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Unity Inova 300 (Varian, Darmstadt, Germany), at 298 K at 300 and 75 MHz (nominal frequency), respectively, in dimethyl-*d*₆ sulfoxide (DMSO-*d*₆). Chemical shifts are given in δ (parts per million) relative to tetramethylsilane (TMS).

Infrared attenuated total reflection (IR-ATR) spectra were recorded on a Avatar 320 E.S.P. Fourier transform IR spectrometer (FTIR) (Nicolet, Offenbach, Germany).

Melting points were determined on a digital melting point apparatus model 8100 (Electrothermal, Southend-on-Sea, U.K.) and are not corrected.

Irradiation Experiments. In a typical experiment, 3.1 mmol/L (1.00 g/L) of phosmet was dissolved in the respective solvent and degassed with nitrogen to prevent solvent oxidation, especially in the case of cyclohexene. Subsequently, the solution was irradiated for up to 7 h while stirring in water-cooled 40 mL quartz cuvettes (60 × 35 mm) with Teflon caps. Irradiation source was a metal halogen lamp (SOL 500, Dr. K. Hönle GmbH, Martinsried, Germany; 120000 lx, 900 W/m²) with a UV filter (WG 295, Schott Glaswerke, Mainz, Germany). Samples of 0.5 mL were taken, diluted with methanol, and used for HPLC analysis.

Irradiation on surfaces and in films was performed by employing a suntest CPS+ (Heraeus-Industrietechnik, Kleinostheim, Germany; xenon lamp, UV filters and air cooling, irradiance at 250 W/m², standard black temperature of 35 °C). For irradiation experiments on glass surfaces, Petri dishes (diameter = 9 cm, without top) and, as silica gel surfaces, TLC plates (silica gel 60, 20 × 20 cm F₂₅₄ Merck, cut to 5 × 5 cm, cleaned up with methanol once before use) were used. Per sample, 1 mg of phosmet, dissolved in 0.1 mL of methanol, was placed on both the glass surface and the silica gel surface. The solvent was evaporated, and the samples were irradiated for up to 48 h. For sample preparation, Petri dishes were rinsed with 25 mL of methanol; the silica gel coating was scraped off and extracted with methanol.

Isolation of Photoproduct 5. The unknown substance formed during irradiation of phosmet in 2-propanol was isolated as follows. Phosmet (300 mg) was dissolved in 300 mL of 2-propanol and irradiated in aliquots of 25 mL for 15 h each. Photolysis mixtures were combined and evaporated to dryness, and the unknown photoproduct was isolated by silica gel column chromatography (eluent light petroleum/diethyl ether 50:50; the first fraction contained the photoproduct) and subsequent preparative HPLC. Methanol was removed in the vacuum, and the remaining aqueous solution was lyophilized, yielding 5 mg of colorless crystals. Purity control was carried out by HPLC analysis (220 nm). The spectroscopic properties agreed with the proposed structure of *N*-isopropoxymethylphthalimide [¹H NMR (DMSO) δ 1.22 (6H, d, CH₃) 3.81–3.67 (1H, sep, CH), 5.00 (2H, s, CH₂), 7.89–7.98 (4H, m, Ar-H); ¹³C NMR (DMSO) δ 123.78, 131.67, 135.18 (s, Ar-C), 167.94 (s, C=O), 69.95 (s, CH₂), 65.12 (s, CH), 22.36 (s, CH₃); MS ESI, *m/z* 220 ([M + H]⁺), 160 ([M - 2-propanol]⁺), 237 ([M + NH₄]⁺), 258 ([M + K]⁺); IR (ATR) (cm⁻¹) 2955, 1777, 1721, 1587, 1438, 1410, 1350, 1327, 1208, 1175, 1077, 991, 729].

Quantification of Phosmet and Photolysis Products. Quantification was performed using external standardization at 220 nm as all measured substances have absorption maxima near 220 nm. Calibration curves were created for phosmet, *N*-methylphthalimide, *N*-methoxymethylphthalimide, *N*-hydroxymethylphthalimide, phosmet-oxon, and phthalimide. *N*-isopropoxymethylphthalimide was quantified by one-point calibration.

Scheme 1. Photoproducts Observed during Irradiation Experiments of Phosmet in Different Solvents [Phosmet (1), Phthalimide (2), *N*-Hydroxymethylphthalimide (3), *N*-Methoxymethylphthalimide (4), *N*-Isopropoxymethylphthalimide (5), and *N*-Methylphthalimide (6)]

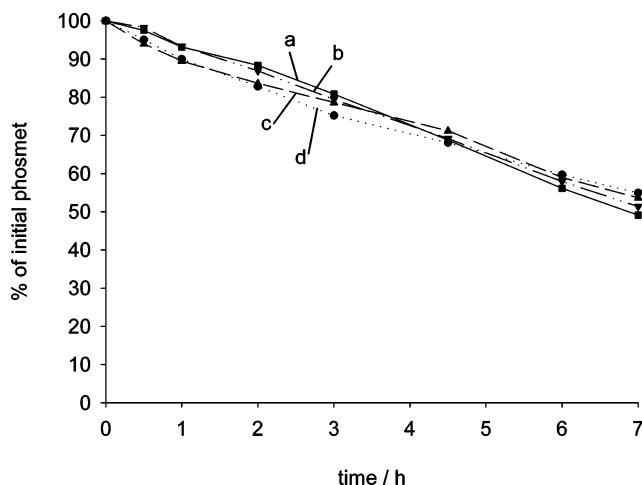
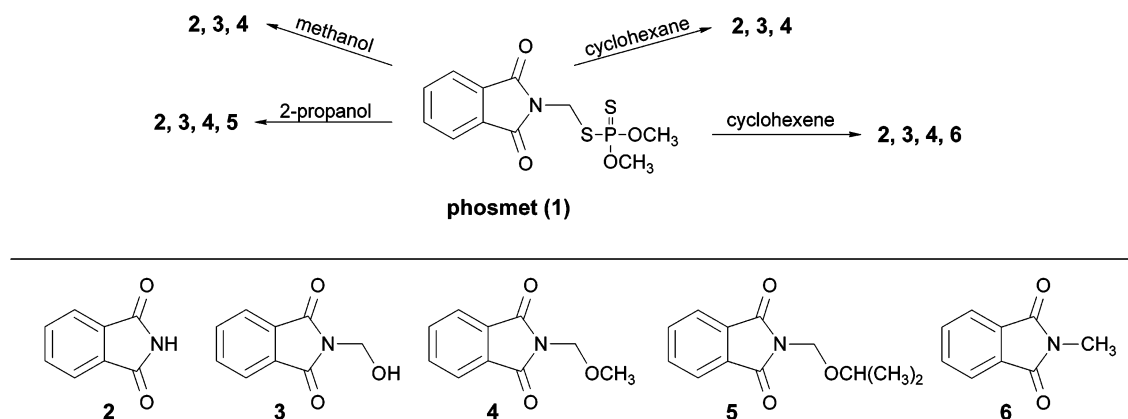


Figure 2. Photodegradation rates of phosmet in four different model solvents, percent of initial phosmet concentration [methanol (a, ■); 2-propanol (b, ▼); cyclohexane (c, ▲); cyclohexene (d, ●)].

RESULTS

Irradiation Experiments in Solutions. Phosmet was readily degraded by UV irradiation (>300 nm) in the four model solvents used (methanol, 2-propanol, cyclohexane, and cyclohexene, 1.00 g/L phosmet) as shown in **Figure 2**.

Unexpectedly, in each of the solvents used degradation rates were found to be very similar at ~50% after 7 h of irradiation (methanol, 49.1 ± 1.5%; 2-propanol, 51.3 ± 0.7%; cyclohexane, 53.7 ± 1.1%; cyclohexene, 54.9 ± 0.3%). Consequently, the half-life period of phosmet averaged to ~7 h. Blank values, measured from samples of the same concentrations as irradiated samples but kept in the dark (same temperature, same period of time), showed no degradation at all.

Even though the degradation rates of phosmet in the model solutions used were very similar, the compositions of photodegradation products were varied (**Scheme 1**).

During irradiation of phosmet in methanol, the photodegradation products phthalimide (**2**), *N*-hydroxymethylphthalimide (**3**), and *N*-methoxymethylphthalimide (**4**) were obtained. Those products were also obtained from hydrolysis experiments (data not shown); **2** (**18**, **19**) and **3** (**19**) have been described as hydrolysis products before.

During irradiation in 2-propanol, the photolysis products **2–4** also appeared, and additionally one more peak was detected at higher retention times than the other photoproducts but at lower retention time than the parent phosmet. The UV spectrum

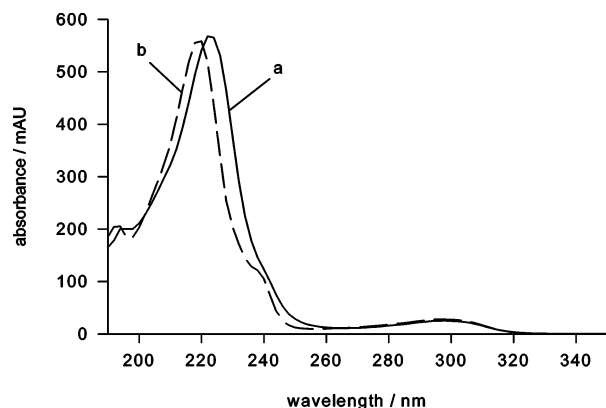


Figure 3. UV spectra (methanol) of (a) phosmet and (b) *N*-isopropoxy-methylphthalimide (DAD spectra).

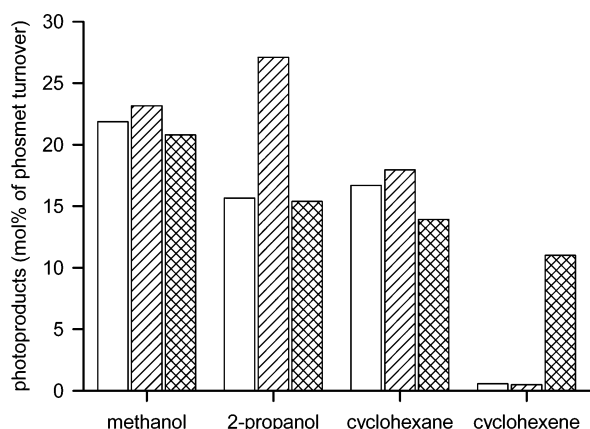


Figure 4. Photoproduct distribution of phosmet turnover after 7 h of irradiation in different solvents: 2 (white bars); 3 (slashed bars); 4 (cross-hatched bars).

showed absorption bands typically for the phthalimide chromophore (Figure 3). After isolation from the reaction mixture, the proposed structure of *N*-isopropoxymethylphthalimide (5) could be verified by MS and NMR measurements. 5 was formed in 2-propanol up to 6.45 mol % after 7 h of irradiation (mole percent of phosmet turnover).

The irradiation experiments in cyclohexane showed the same products found in methanol. During irradiation of phosmet in cyclohexene, 2–4 were also obtained, but the concentrations of all three components were significantly lower as compared to the other solvents. Additionally, small amounts of *N*-methylphthalimide (6) were identified, and many yet unidentified products were found during RP-HPLC analysis at later retention times than the parent phosmet. Furthermore, the sum of derived photoproducts was substantially lower than the sum of photoproducts in the other solvents, which denotes that phosmet must have partly reacted in a different way. Formation of phosmet-oxon (7) during irradiation was near or below the limit of detection in all four solvents.

Figure 4 shows the distribution of the three main photolysis products (2–4) of phosmet in the different solvents after 7 h of irradiation. The amount of 2 occurring in cyclohexene during irradiation was very low in comparison to the amounts measured in the other model solutions. The highest amount of 2 was obtained in methanol (21.9 ± 1.5 mol %).

Likewise, the formation of 3 in cyclohexene was also very low, whereas the highest yield of 3 could be measured in 2-propanol (27.1 ± 1.1 %). 4 was observed in amounts of 11.0–

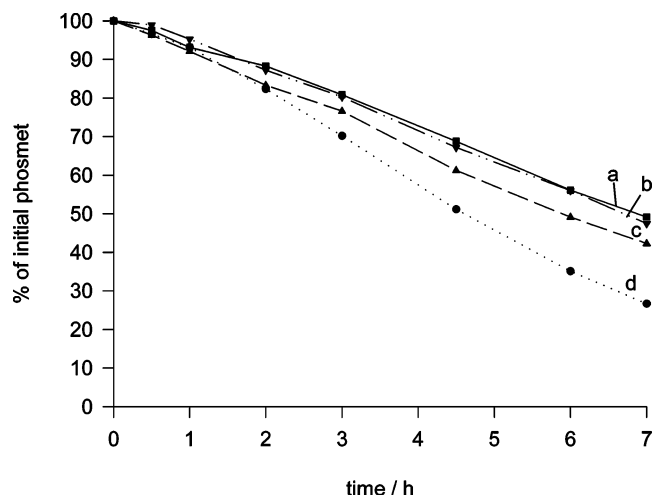


Figure 5. Photodegradation rates of phosmet in methanol with different percentages of water [methanol (a, ■); methanol/10% (b, ▼); methanol/20% (c, ▲); methanol/30% (d, ●)].

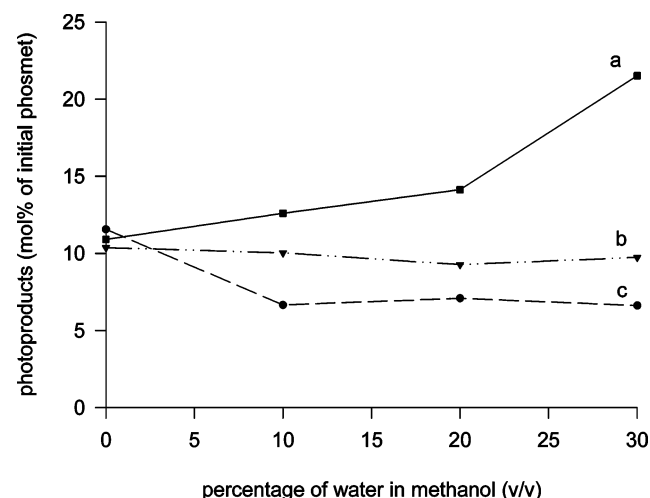


Figure 6. Dependency of water percentage of methanol and formation of the photoproducts 2 (a, ■), 3 (c, ●), and 4 (b, ▼) after an irradiation time of 7 h.

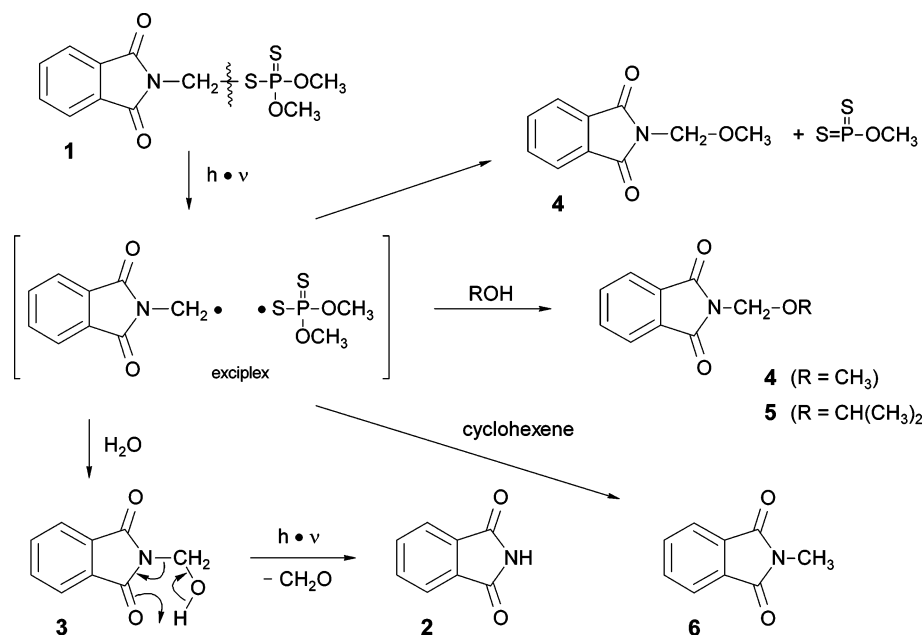
20.8% in all model solutions, with lowest values in cyclohexene and highest in methanol.

As the observed reaction products are also formed in hydrolysis reactions, further irradiation experiments in methanol were carried out with various percentages of water [10, 20, and 30% (v/v)]. Figure 5 shows the photoinduced degradation as a function of the solvent composition. Once again, degradation was not detectable in un-irradiated samples.

Up to a percentage of 10% water, no increased degradation was detectable, but starting with 20% water, an increased degradation took place, and, at a water percentage of 30%, merely 26% of the initial phosmet was left after 7 h. Simultaneously, the formation of 2 was strongly increased with higher water percentages (Figure 6). The impact of water on the formation of 3 showed a small decrease between 0 and 10%, but had no more effect between 10 and 30% of water. The occurrence of 4 seems to be independent of the presence of water as in all cases with up to 30% of water, from 9.0 to 10.2 mol % of the initial phosmet was obtained.

Irradiation Experiments on Surfaces. Some irradiation experiments on surfaces were carried out to study the photochemistry of the pure nondissolved active agent in interaction with air contact (oxygen).

Scheme 2. Proposed Mechanisms of the Formation of Photoproducts of Phosmet during Irradiation



Glass surfaces were chosen as a relatively inert material (droplets on glass surface); silica gel plates offer a surface for good interaction possibilities between phosmet and air.

The product spectrum after irradiation on silica gel plates for up to 48 h (19% of degradation after 6 h, 73% after 48 h) included **2**, **3**, **4**, and **7**. Whereas products **2**, **3**, and **7** have already been identified in earlier studies on silica gel plates (5, 20), **4** could additionally be detected in this study. After 6 h, photoproducts **2**, **4**, and **7** were measured in amounts of 66, 22, and 4 mol %, respectively. After 48 h, 59, 2, 34, and 4 mol % of **2**, **3**, **4**, and **7**, respectively, were obtained (mole percent of phosmet turnover).

During irradiation studies on glass surfaces, a higher degradation rate than on silica gel plates was found (32% after 6 h; 95% after 48 h). During these experiments very few degradation products were obtained. Only small amounts of **7** were determined; the photoproducts **2–4** could not be detected.

DISCUSSION

Unexpectedly, the degradation rates of phosmet in the presence of the four different solvents used were determined to be nearly independent of the chemical environment. Former studies with different pesticides such as parathion (8) or folpet (21) showed an increased degradation in the presence of olefins as compared to alkanes or alcohols. However, in contrast to phosmet, these pesticides have chlorine atoms or nitro groups as part of the molecular structure, which are known for fast and effective reactions under irradiation conditions, for example, dechlorination and nitroreduction (7, 22).

Concerning the mechanisms of photoproduct formation, bond cleavages around the phosphorus dithioate group are generally favored, being partly influenced by the solvent environment. Thus, the photoproduct **5** has to stem from intramolecular reactions between phosmet and the isopropanol solvent (photosolvolysis) (Scheme 2), being the only possible source for isopropoxy moieties, and, consequently, was not found in the other solvents. During irradiation in methanol, the same solvolysis mechanism can be discussed for the formation of **4** (Scheme 2). However, in the presence of cyclohexane, cyclohexene, or 2-propanol, **4** can only be understood as a result of

intramolecular rearrangements from split-off thiophosphate groups (**3**), presumably starting from an exciplex. Cleavage of the sulfur–carbon bond, followed by hydrogen transfer, led to **6**, whereas a hydroxyl transfer in terms of photohydrolysis through traces of water yielded **3**. However, during the methanol/water experiments, **3** was reduced slightly rather than increased, and phthalimide (**2**) became the main product. Assuming that **3** will nevertheless be the first and main product during methanol/water irradiations, UV radiation will also be mainly absorbed by **3**, enforcing further degradation reactions which can easily be explained by a six-membered ring McLafferty-type rearrangement with scission of formaldehyde (Scheme 2). A separate irradiation experiment with **3** in cyclohexane resulted in **2** as the only photoproduct, which was not formed in nonexposure experiments, whereas Khan (23) described **2** as a hydrolysis product of **3** under alkaline conditions.

During irradiation in cyclohexene, *N*-methylphthalimide (**6**), which is reported to be one of the main photolysis products in diethyl ether along with *N*-methoxymethylphthalimide (**4**) (3), could be identified as a minor photolysis product in concentrations of up to 2.8 mol % (after 6 h of irradiation, mole percent of initial phosmet). **6** could not be identified in any other of the solvents used. As the sum of identified photoproducts in cyclohexene was substantially lower as determined in the other solvents used, and many yet not identified products were found at later retention times during RP-HPLC, phosmet must have reacted in a different way as well. In addition to extensive photodecomposition, photoaddition reactions with cyclohexene can be assumed from our own experiences. Products of the well-known olefin/phthalimide photochemistry (24) were also observed during earlier irradiations of the fungicide folpet and other *N*-substituted phthalimides (25) in the presence of cyclohexene or methyl oleate.

Whereas the nitrogen-purged solvents were not absolutely free of oxygen, the irradiation experiments on surfaces clearly showed only a slight influence of oxygen on phosmet photodegradation. The typical photooxidation-derived oxon derivative (**7**) was found only in very small amounts. Product **3** was found to be the major product in solutions, but only a minor constituent after surface experiments, whereas **2** was determined to be the

main product. Evaporation, which was partly observed during irradiations on glass surfaces only, was not taken into account.

Recapitulating, in model environments providing different functional groups phosmet was readily photodegraded, yielding phthalimide derivatives mostly with the loss of the dithiophosphorus group. Additionally many not yet identified photoproducts were formed in cyclohexene, which are supposed to be photoaddition products. With the understanding of general photodegradation principles, in vitro and in vivo irradiation experiments in the presence of wool wax/skin lipids have to be performed and will be undertaken in the next step.

ACKNOWLEDGMENT

We thank S. Mika (Institute of Chemistry, University of Hohenheim) for recording the NMR spectra.

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Received for review March 14, 2003. Revised manuscript received July 29, 2003. Accepted August 1, 2003.

JF034253Y