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Kinetics and Photophysical Mechanism of Sunlight Photolysis of Unstable Resmethrin and Phenothrin in Aerosols and Thin Films

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Negative ecological consequences of insecticide applications are often assigned to their persistence in biosphere. Due to long residence time of insecticides in plant, soil, water, and air they are dangerous for people and environment. It would be desirable to use the photounstable insecticides having short residence time in air and on the surface of leaves or soil. However, these insecticides are unsuitable for the methods of aerial and ground spraying. In this case a dispersed insecticide first precipitates on plants to form a deposit. Only then insects may come into contact with the deposit, accumulate a lethal dose, and die. For a number of reasons, a period of accumulation covers many hours, and even a few days. Evidently, the insecticides that quickly decompose under sunlight, cannot be used. However, these insecticides may be quite good for the Optimum Aerosol Technology (OAT) of insecticide application (Koutzenogii 1981, 1989). In this case, a lethal dose is accumulated not at a prolonged contact with a deposit but upon a selective hit of aerosols directly on insect bodies just during the wind drift of aerosol cloud across the treated field. The main peculiarity is that each concrete case (kinds of insects and plants, landscape and meteorological conditions, etc.) needs aerosols of a certain optimum size (within 1-25 µm), which provides a relatively selective hit of particles on pest insects, rather than on plants and soil. Due to the processes of wind drift of aerosols in a stable stratified atmospheric surface layer, aerosol treatments are performed at night only. The night treatment must cause aerosol accumulation of a lethal dose and, hence, the mortality of pest insects. However, next day the aerosols precipitating on plants,soil, and dissipated in air could fast photolyze under sunlight. It may be assumed then, that the photolabile insecticides could be used as aerosols in plant

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protection (Samsonov et al. 1994).

Such insecticides as resmethrin and phenothrin are likely to be of a major importance. They are produced commercially, exhibit high efficiency when applied to insects, but possess a low mammalian toxicity. They are known to decompose under sunlight. The photolysis of resmethrin and phenothrin was studied in solutions and films (Ueda et al. 1974, Ruzo et al. 1982, 1985). Photolysis of the above insecticides in aerosols was not studied. It is noteworthy that there is a lack of investigations on photochemistry of pesticides as aerosols. At the same time, a substantial part of pesticides in atmosphere exists in the aerosol state. The ingress of pesticide particles into air takes place both during the plant protection and due to the adsorption of pesticide vapours on atmospheric aerosols. The effect of the aerosol state on the rates and pathways of pesticide photodestruction could be significant. First, the sunlight absorption by aerosols depends on particle size. Second, the diffusion rates of reactive molecules within particle bulk are determined by sizes. Third, as a rule, pesticides are used in plant protection as multiingredient solutions. The evaporation of some particle ingredients can transform the particle state from liquid to solid. Thus, the above diffusion rates must sharply decrease. The paper gives the rates, quantum yields, and the primary photophysical processes of sunlight photolysis of resmethrin and phenothrin in aerosols and thin films.

MATERIALS AND METHODS

The liquid commercial formulations of resmethrin (Isathrin 10 % e.c., Roussel Uclaf) and phenothrin (Sumithrin 10% e.c.,Sumitomo) were used. Their acetone solutions (10-50 mg of active pesticide ingredient per mL) were applied with a pipette (0.05-0.2 mL) on glass plates (2.7* 7.5 cm^2). After full evaporation of acetone and volatile ingredients (1-3 hr, at room temperature) the films formed (0.03-1 mg cm^{-2}, i.e. 0.3-10 µm thickness of active ingredient, but 3-100 µm overall thickness of the above formulation). Gas-liquid chromatography (glass column, 40 cm*3 mm, 5% SE-30, Chromaton-N-AW-DMCS, 0.16-0.2 mm, 40 mL min^{-1} of argon 175°C-10°C min^{-1}-225° C) was used to record resmethrin, phenothrln, permethrin (without their isomer separation). Flame ionization and electron capture detectors were used. The experiments were performed under sunlight, in summer, near Novosibirsk (55°N). In each experiment some glass plates (8-12) with films were exposed to solar irradiation. Before and periodically during the photolysis 2-3 plates were taken away, the films were washed off with acetone or hexane for chromatography. The photolysis of aerosols was performed in an aerosol chamber 30*30*40 cm^3. One of the chamber walls, facing the sun, was made of UV transparent polyethylene film. Aerosols were produced from the above commercial formulations using a glass pneumatic sprayer of the Collision type (Green & Lane 1964). The air+aerosols flow entered the chamber through a rubber tube. Particle size distribution was the known “log-normal” one with a mass-median diameter

d_m=2 µm and standard deviation $\sigma g=d_{84}/d_m=d_m/d_{16}$=1.8. Hence, 68% of substance were contained in particles from 1.1 µm (d_m/σ_g) to 3.6 µm ($d_m*\sigma_g$), and 95% from 0.6 µm (d_m/σ_g^2) to 6.5 µm ($d_m*\sigma^2$). Working mass concentrations were varied from 0.1 to 1 mg L^{-1}; particle concentrations were $3*10^7$ - $3*10^8 L^{-1}$. It was impossible to maintain a steady aerosol concentration in chamber due to precipitation of particles on the bottom and walls (3-6 times an hour). This process could artificially disturb the kinetics of aerosol photolysis. Therefore, the above spraying of unstable isathrin was accompanied by simultaneous spraying of photostable permethrin (Ambush 5%, ICI). Thus, a decrease of the resmethrin/ permethrin ratio in the aerosol mixture of the above substances before and after solar irradiation characterizes just the photolysis rate of unstable resmethrin independently of simultaneous aerosol precipitation. For chromatographic measurements of the above ratio a sample of aerosol mixture was pumped out from the chamber through aerosol thin-fibrous filters before (0.5 min, 6 L min^{-1}) and after photolysis (10 min). However, the method is unsuitable for phenothrin aerosols because their photolysis takes 2-4 hr (against 0.5-1 hr for resmethrin) and a large loss of aerosols due to precipitation occurs. In this case, the photolysis of phenothrin aerosols, previously precipitated on glass plates, was studied.

RESULTS AND DISCUSSION

According to preliminary experiments, the films undergo very little decomposition and evaporation in the dark (less than 3%, i.e. to within chromatography accuracy). Figs.1 and 2 show the photolysis kinetics of insecticide films with 3-7 µm overall thickness at the day-time. The data are represented as the first order process $M(\mathbf{t})=M_0*\exp(-\mathbf{k}*\mathbf{t})$, where M_0 and $M(\mathbf{t})$ are the initial and current masses of insecticide on the plates; **k** is the photolysis rate constant (hr^{-1}). It is observed (lines 3-8, fig.1; 1-3, fig.2) that the first order of photolysis holds for a deep degree of insecticide decomposition. Thus, one can readily use the same form of data in the experiments when only two measurements are possible (in aerosol chamber or in the oxygen-free boxes before and after photolysis, fig.3). The data representation in plots rather than in tables is justified enough and visually more informative. The rates of resmethrin degradation are large. The quantity of resmethrin can decrease 3-20 times an hour depending on the zenith angle and atmospheric conditions. The photolysis rates of phenothrin are lower. It is assumed, however, that when used for plant protection the resmethrin and phenothrin aerosols could photolyze during the day.

The quantum yield of resmethrin film photolysis was determing using the well-known ferrioxalate actinometer to measure the intensity of the line λ=313 nm induced by a high-pressure mercury lamp. The selection of this line was provided by a water heat filter (thickness 10 cm, quartz windows), of the UV and yellow glass filters (UVG-2, 3 mm; YG-3, 2 mm, USSR). The measured quantum yield is (φ=0.38± 0.08. This value is likely to be under-

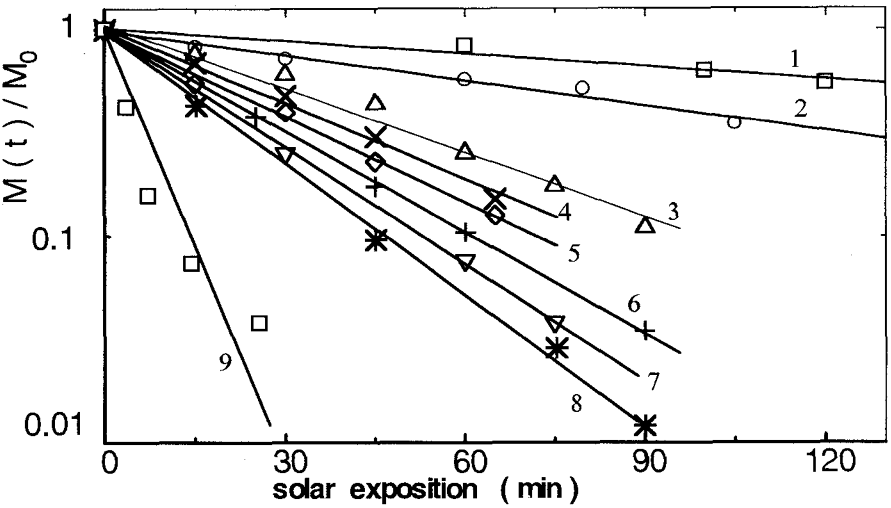

Figure 1. The first-order kinetics of sunlight photolysis of resmethrin (isathrin) films on glass plates: at the morning (1,2); at the forenoon (3,4); at the midday (5,6,7,8); "isathrin +methylene blue" mixture, (9, midday).

estimated because the light absorption by isathrin film was determined by both resmethrin itself and a slight absorption of other isathrin ingredients. Moreover, it was possible to estimate the overall quantum yield of sunlight photolysis (300-360 nm) using the rate constants (fig.1, midday), the recorded absorption spectrum of isathrin film and solar irradiance. The available relations and data were used to calculate solar actinic irradiance, taking into account the height, season and region distributions of ozone, its UV absorption, the Reyleigh and aerosol light scattering in atmosphere, the sun zenith angles, etc. (Leighton 1961; Makarova et al. 1991; Komarov et al. 1988). The calculation (omitted here) gives $\varphi = 1.0 \pm 0.4$. The value $\varphi \geq 0.38$ is large enough and the conclusions will be drawn below on a possible photophysical mechanism. The quantum yield for phenothrin film was measured to be $\varphi = 0.1 \pm 0.05$ which is close to that the previous one ($\varphi = 0.07$, Ruzo et al. 1980).

As mentioned above, the photolysis of resmethrin and phenothrin has been studied in solutions and films (Ueda et al. 1974; Ruzo et al. 1982, 1985). It was shown that the photooxidation of resmethrin was the main primary pathways of the overall process. However, a substantial amount of chrysanthemic acid was found as a photoproduct which may serve as an evidence for a partial direct decay of excited resmethrin molecules into fragments. To measure quantitatively the efficiencies of the above pathways the comparative photolysis of resmethrin in the aerosol chamber with oxygen or oxygen-free media (air or argon) was performed. As follows from fig.3 (lines 1 and 4; 2 and 8) the rates in the oxygen-free medium are about 12-15 times lower. The photolysis of phenothrin in degassed benzene

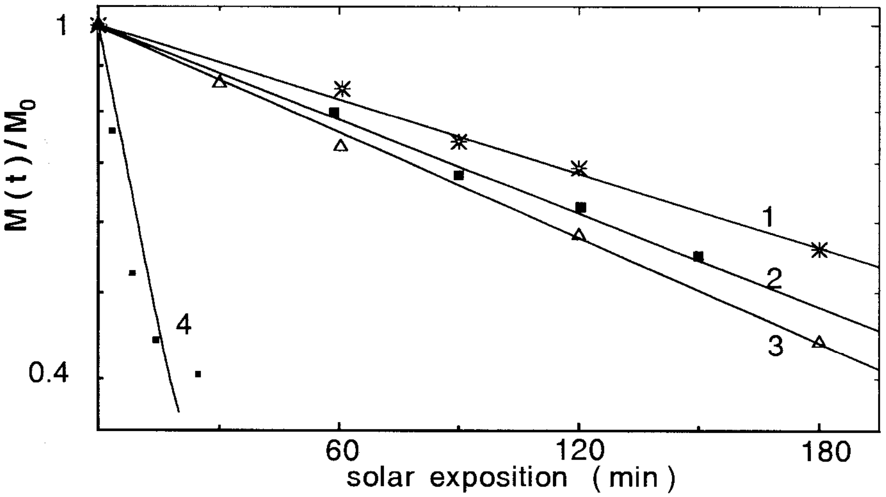

Figure 2. The photolysis of phenothrin (sumithrin) films: at the forenoon (1); at the midday (2, 3); sumithrin+methylene blue mixture (4, midday).

solution also testifies to a 10-times decrease of the rate (Ruzo et al 1982). It may be concluded that initially the photolysis of resmethrin and phenothrin results in their oxygenation. A direct decay of excited molecules into fragments is no more than 7-10%. Addition of oxygen to a resmethrin molecule raises the problem of the dependence of photolysis rate and, probably, of mechanism on the film thickness (aerosol diameter) and phase state. It can be calculated that oxygen, initially dissolved in a film, is insufficient for full oxidation of resmethrin (0.1-1% of required amount) and its diffusion from outside is necessary. The dependence of photolysis rate on film thickness has been examined for isathrin films from 10 to 100 μm. The rate constants were **k**=1.3 hr^{-1} for the film with thickness of 10 μm, **k**=1.2 hr^{-1} for 40 μm, and **k**=0.75 hr^{-1} for 100 μm. Although the rates somewhat decrease with increasing thickness, this has no connection with oxygen diffusion. In this case, one could expect a hundredfold decrease because the diffusion rate is proportional to D/L^2 (L is the film thickness; D is the diffusion coefficient of oxygen intra the film). The reason for a slight slowing down of k is the weakening of UV-light due to its absorption in thick films (isathrin film of 10 μm absorbs ~5-10% of light, a one of 100 μm - up to 50-60%). As follows from fig.3, there is no marked difference in the rates for aerosols and films. The reason for this independence is the low absorption of actinic sunlight by films and aerosols of the above sizes. The absence of an effect of the aerosol state on the photolysis rates of isathrin testifies also that during experiments (1-10 hr) the films and aerosols remain in the liquid state because in liquids only the diffusion coefficients are large enough to provide fast oxygen intake. The solid state could sharply decrease the oxidation pathways of the above films and aerosols on the plates, in air,

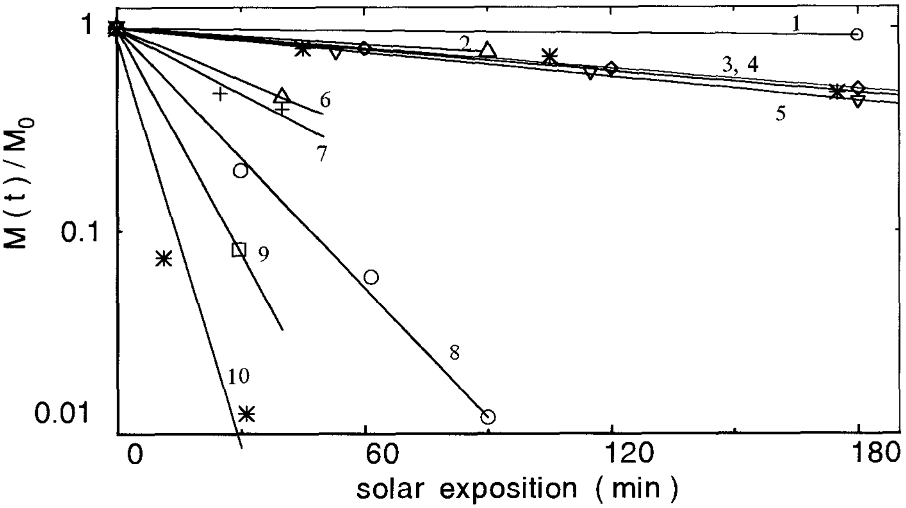

Figure 3. The comparative photolysis : a) sumithrin films in oxygen-free (1) and oxygen (4) media; b) isathrin films in oxygen-free (2) and oxygen (8) media; c) phenothin as precipitated aerosols on plates (3) and as films (5); d) isathrin as aerosols (6) and as films (7); e) isathrin +methylene blue mixture as aerosols (9, midday) and films (10, midday).

and on plant surface. Surprisingly, the isathrin aerosols remained quasi-liquid because the preliminary experiments using a capillary gas chromatography, have showed the disappearance of the majority of isathrin ingredients due to their evaporation. On the other hand, after evaporation of liquid solvents, the aerosols are known to remain sometimes as quasi-liquid ones that are oversaturated with a pesticide ingredient. This effect was observed for the "DDT + diesel oil" formulation during aerosol treatments of forests (Kovalskii et al. 1978). The same case is probable for isathrin formulation. The hindrance of diffusion ways could be the reason for the differences in the rates and products of resmethrin photolysis in the different studies (Ueda et al. 1974 and cited there). Pure resmethrin was used there and the films must be solid. It is likely that of major importance would be the porosity and friability, through which the oxygen can penetrate into the film and particle bulk.

A high value of quantum yield for the photolysis of resmethrin should be explained. Note, that the primary pathways are the reactions with oxygen, i.e. bimolecular processes. The distribution of oxygen molecules dissolved in isathrin, is such that in any direction there are 5-10 resmethrin or other ingredient molecules per oxygen one. The time of oxygen diffusion in liquid over 5-10 intermolecular distances is estimated to be 10^{-7}-10^{-8} sec. Since the value $\varphi \geq 0.38$ means that actually each excited molecule reacts with the oxygen one, the excitation lifetime must be greater than 10^{-7}-10^{-8} sec.

In a liquid, the singlet excitation cannot be retained for so long. However, some kinds of molecules are known to exist over prolonged periods in the triplet states which they enter from the singlet ones. In (Foote 1968, Calvert&Pitts 1966; Gollnick 1968) the mechanism of photooxidation of such compounds has been considered. It is connected with the intersystem crossing of singlet into triplet. The molecule preserves this state till the approach of the oxygen one. Their interaction results in oxygen excitation into the singlet state. Thereafter, the singlet oxygen reacts with the surrounding molecules. The ability ,e.g. of furan derivatives to react with singlet oxygen is very high, so that the quantum yield tends to unity ($\varphi = 0.76$ for dimethylfuran, cited by Gollnick 1968). It may be assumed that a similar mechanism holds for resmethrin and phenothrin photolysis. This is verified by the existence of furan ring in resmethrin molecule, the participation of oxygen in photolysis, and the large quantum yield. In (Ueda et al.1974, Ruzo et al. 1985) the like conclusions have been drawn on the possible photolysis pathways those were similar in photooxidation of furans.

The intermediate triplet excitation of resmethrin molecules makes it possible to slow down the photolysis rate. To this end, the substances that can quench the triplets, should be added to resmethrin formulation. These experiments were carried out using dimethylaniline (DMA, a quencher of triplets, Gollnick 1968). Mixing it with isathrin (60-100% of resmethrin amount) we have slowed down the rates 5-10 times. DMA is not an ideal inhibitor due to both its volatility and eigen photolability. The substances for photolysis inhibition upon their actual application in plant protection together with triplet quenching must be as nonvolatile as insecticide itself. In addition, they must be harmless for people and environment. Probably, β-carotene could be used (Foote 1968). Note, that Ueda et al. (1974) have failed to prolong the persistence of resmethrin by formulating it with a few UV screening agents and antioxidants. Margulies et al. (1993) described the effective photostabilization of resmethrin and other pesticides, coadsorbed on clays and chromophores together with energy or charge acceptors. The main mechanisms of stabilization include energy transfer and steric hindrance, rather than direct triplet quenching. On the other hand, adding some substances to photogenerate singlet oxygen molecules (Methylene Blue,MB, Bengal Rose,BR, etc.) one could to accelerate the photodestruction of some pesticides. Mixing these substances with isathrin and sumithrin (25-80% of insecticide amounts) we have observed at least a 3-10-fold increase in the rates (figs.1-3). These sensitizers are poorly soluble in the above formulations. The films and aerosols were observed with a microscope as the quasi-solid heterogeneous ones. The heterogeneity and fast photodestruction of MB are the reasons for a poor reproducibility of rate constants (fig.1-3). The usage of BR or MB as photosensitizers is well-known in laboratory studies. However, the above and other sensitizers could be used actually in the OAT to provide fast destruction of isathrin and sumitrin aerosols precipitated on plants, just in the morning after night aerosol treatment, e.g. to prevent potential death of bees.

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