

Photolysis of Organophosphorus Fungicides

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Pesticides applied for the protection of crops are decomposed or transformed in the environment by the biological factors such as microorganisms and plants as well as physicochemical factors such as sunlight, heat and air. Among these factors, the sunlight is one of the most important factors. Sunlight possesses sufficient energy to cause photochemical transformations or decompositions in organic pesticides. There have been found a number of photoproducts which are more persistent in the environment and are more harmful to the mammals or insects than their original compounds. Therefore, from the view point of chemical alteration of pesticides in the environment and effects of the altered products on ecosystem, the investigation on photolysis of pesticides is of great importance in the pesticide research.

At the same time, the research of photolysis may lead to the development of safer and more efficient use of pesticides. Recently, attempts have been also made to remove the pesticidal residue from the crop by irradiation of ultraviolet light. In addition, it is often observed that metabolites in the biological process coincides with physicochemical products by the photoreaction. The research conducted as to photolysis often makes many

important contributions to biochemical research of pesticides.

The author early commenced a study of this subject by using organophosphorus fungicides as test compounds, and has obtained interesting results.¹⁾²⁾³⁾ The important ones among them will be introduced briefly in this paper.

Materials and methods

Test compounds used in this experiment were edifenphos (Hinosan®), Kitazin P® and Inezin®, whose structural formula are shown in Fig. 1. These organophosphorus fungicides were developed as substitutes for organomercury disinfectants for controlling rice blast disease. Since light energy decreases as the light wavelength shortens, the important light region concerning photolysis is ultraviolet region. In this experiment, samples of test compounds were prepared in the three states, aqueous solution, thin film, and n-hexane solution, in order to simulate the actual state of the pesticides in the environment. After samples were exposed to ultraviolet light emitted from the various light sources, resultant photoproducts were separated and identified by isotope tracer technique, chro-

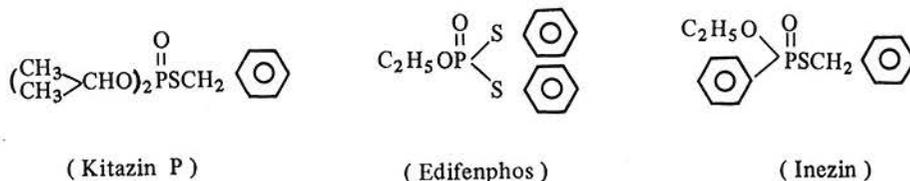


Fig. 1. Test Compounds

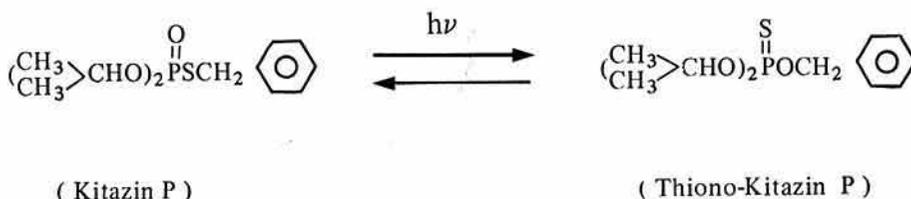


Fig. 2. Photoisomerization

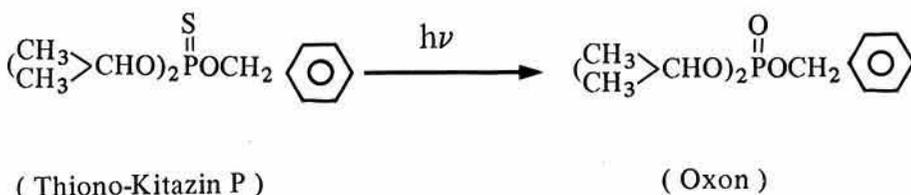


Fig. 3. Photooxidation

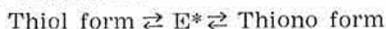
matographic techniques such as thin-layer chromatography and gas chromatography, and various kinds of spectrometries such as infrared spectrometry, mass spectrometry and nuclear magnetic resonance spectrometry.

Photolysis steps and pathways of organophosphorus fungicides

On the basis of the experimental results, the following steps were found as the principal ones in the photolysis of organophosphorus fungicides tested: isomerization, oxidation and reduction, hydrolysis of ester linkage, transesterification, and addition of solvents.

As shown in Fig. 2, photoisomerization was observed in Kitazin P and Inezin, both of which are S-benzyl esters. However, in case of edifenphos which contains S-phenyl group, such isomerization never occurred and it was considered that this reaction was specific in S-benzyl esters. This isomerization was strictly concerned with the wavelength of light. As the wavelength increased, this isomerization remarkably decreased and it was slightly observed in the light region over than 350 nm. On the other hand, when thiono type of Kitazin P (thiono-Kitazin P) was exposed, reverse isomerization from thiono form

to thiol form was observed. These results indicate that the following equilibrium exists between thiol form and thiono form on ultraviolet irradiation.

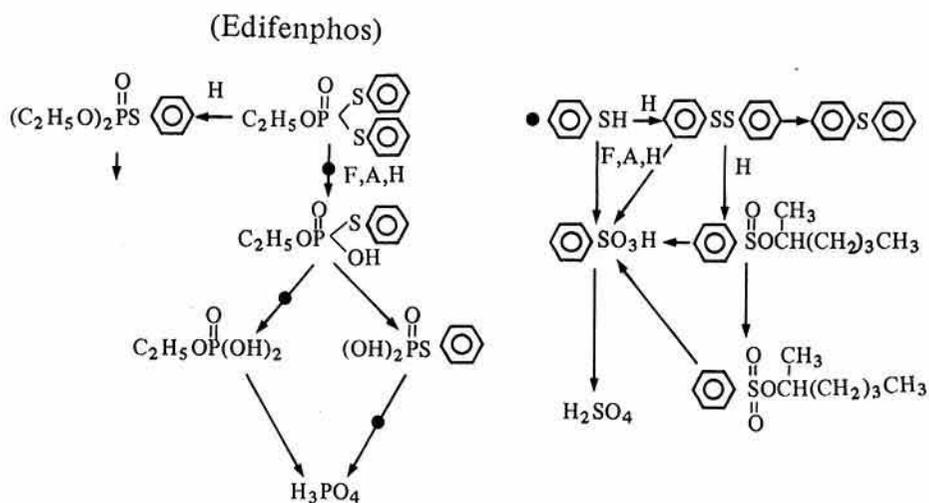


(E*: excited state of thiol or thiono form)

However, the reverse isomerization from thiono form to thiol form was not detected in the case of Inezin. This fact might be attributed to that the equilibrium shown in above equation is shifted to the side of the thiono form.

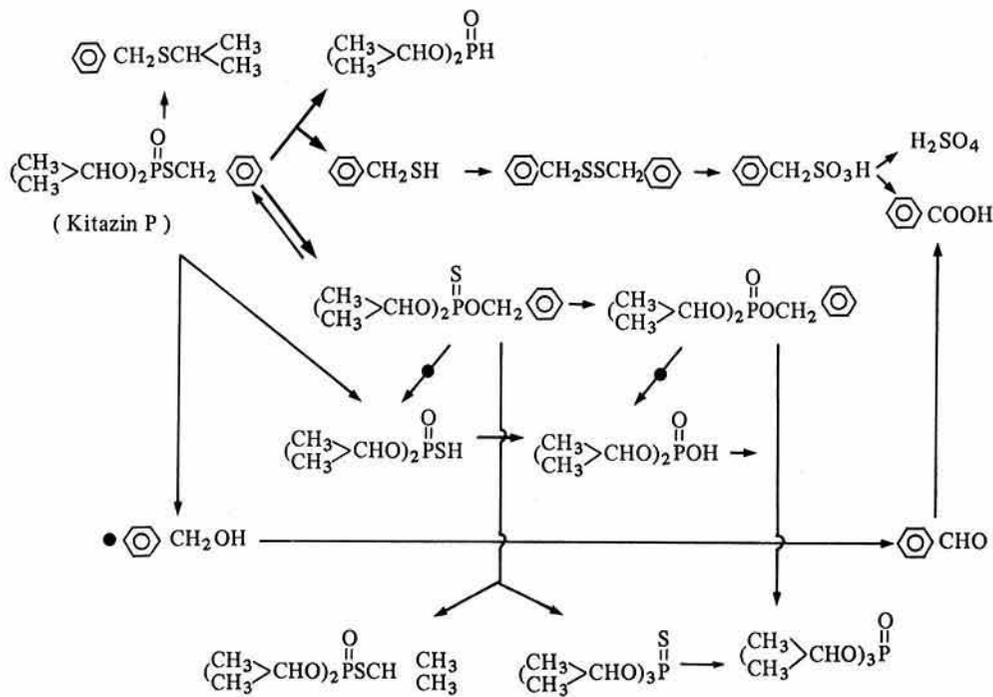
Photooxidation are often observed in photolysis. Thiono-Kitazin P and thiono-Inezin produced by isomerization were oxidized to form their oxons, as seen in Fig. 3. In many cases, oxon types are more harmful to the mammals and insects than their thiono types. From the view point of environmental toxicology, this kind of oxidation process in photolysis is a very important change.

The cleavage of P-S bond by ultraviolet light gave phenylthio radicals or benzylthio radicals which were readily oxidized to produce benzoic acid or sulfuric acid via corresponding disulfides and sulfonic acids. In Kitazin P and Inezin, benzyl alcohol was formed by the cleavage of ester linkage, and it was also oxidized to benzoic acid via benzaldehyde. On the other hand, reductive



● : the production of thiophenol

Fig. 4. Proposed photodecomposition pathway of edifenphos.
F : film, A : aqueous solution, H : hexane solution.



● : the production of benzyl alcohol

Fig. 5. Proposed photodecomposition pathway of Kitazin P.

cleavage was found in Kitazin P and Inezin. In this case, hydrogen may be derived from any of solvents, original compounds or photo-products.

Photohydrolysis catalyzed by ultraviolet light was recognized in any of test compounds. The first step of this reaction occurred in P-S bond in edifenphos, and in both bonds of P-S and S-C in Kitazin P and Inezin. Successive photohydrolysis occurred in steps from original compounds, finally phosphoric acid in edifenphos and Kitazin P. In case of Inezin, however, all of phosphorus-containing photo-products detected in this experiment retained P-C bond as has been reported for the biological degradation of organophosphonates. This fact may suggest that P-C bond of Inezin is also resistant to physical attacks such as ultraviolet light.

There were found a number of photo-products which were assumed to be due to radical exchange of two molecules on irradiation of Kitazin P and Edifenphos. It may be referred to as transesterification. In either case, however, no compound was found that increased aromatic rings. This phenomenon might be attributed to the difference in stability to ultraviolet light between the products by transesterification. In fact, when the photolysis rate of transesterification products of Edifenphos was compared under ultraviolet irradiation, *S,S,S*-triphenyl phosphorotrithiolate was degraded approximately 25 times faster than *O,O*-diethyl *S*-phenyl phosphorothiolate.

When edifenphos was irradiated in *n*-hexane solution, some phenylthio radicals combined with the solvents to give some adducts in the course of oxidation process. This result demonstrates that the substances coexisting with the pesticides play important roles in photolysis.

On the basis of photoproducts identified in this experiment, photolysis pathways of test compounds were tentatively proposed. Among them, the pathways concerning Edifenphos and Kitazin P are shown in Figs. 4 and 5, respectively.

In conclusion

As mentioned above, the investigation on the photolysis of pesticides is an important research to know the fate of the pesticides in the environment. In the United States, in fact, the data on photolysis are necessary for the safety evaluation of a pesticide. The information obtained in this experiment will also contribute to the prediction of photolysis pathway and assessment of safe use of other organophosphorus pesticides.

If the methods for controlling the photolysis of pesticides are developed, it may be possible to regulate the persistence of them in the environment. As to persistent pesticides, for example, residual period may be shortened by the addition of substances accelerating the photolysis of the pesticides. On the other hand, there are a number of compounds that have not been in field use because of instability to the sunlight, even though they show excellent effectiveness against pests *in vitro* tests and low toxicity to economic species. If it is possible to protect photodecomposition in the field for certain period by some substances, we may be able to obtain ideal pesticides. For this purpose, we are searching substances for accelerating or protecting photolysis of pesticides, and have gotten certain candidate compounds. We will proceed with the investigation of the pesticide photolysis for the practical application of these substances.

References

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