

Photochemical timescales in the degradation of pesticides: direct photolysis of dimethomorph in aqueous solution using polychromatic and monochromatic irradiation

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Dimethomorph is a fungicide of the cinnamic acid type and consists of and is applied as a mixture of Z/E-isomers.

A qualitative rapid photochemical interconversion of isomers has been reported by industry. However, quantitative data of photochemically induced Z/E-isomerisation and lifetimes of irreversible loss processes are not available. Moreover, in general comparisons of quantum yields using polychromatic and monochromatic irradiation were seldom performed.

Besides UV spectra, a comparison of quantum yields in aqueous solution using polychromatic and monochromatic irradiation is reported and discussed. Furthermore, the fast photochemical isomerisation (completed within 2-30 minutes) is compared with the very slow irreversible photochemical loss reaction (lifetime in the range of weeks-months). The kinetic scheme for the photochemical reaction of dimethomorph investigated in this study is shown in Figure 1.

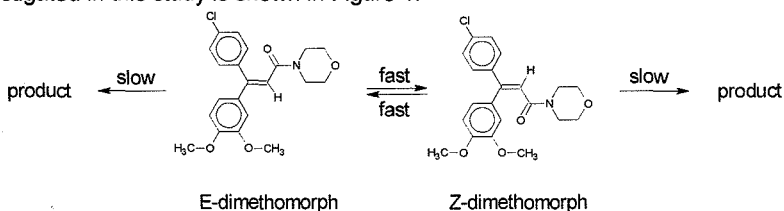


Figure 1: Kinetic scheme of the fast isomerisation and slow irreversible photo reaction of Z- and E-dimethomorph

As known for other compounds of the cinnamic-acid type quantum yields for the photochemical isomerisation of Z- and E-dimethomorph were found to be high. The sum of both quantum yields for polychromatic irradiation and monochromatic irradiation (at $\lambda=340$ nm) are within the error of the experiment $\Phi_{E \rightarrow Z} + \Phi_{Z \rightarrow E} = 1$, indicating the same excited state. Quantum yields for the polychromatic irradiation and monochromatic irradiation were found to be comparable. Rate constants obtained for sunlight irradiation were compared with values obtained from model calculations and were found to be in agreement (deviation below 5%) with theory using monochromatic quantum yields.

As a consequence of the isomerisation reaction sunlight irradiation (in April) increases the start fraction found in the mixture of Z- and E-dimethomorph (Z:E = 1.25:1) in the environment to a fraction of Z:E = 4:1.

A slow irreversible reaction for both isomers was found after more than 150 hours of polychromatic irradiation with lifetimes in the range of one month (sunlight, spring, 50° latitude).