Guthion Half-life in Aqueous Solutions and on Glass Surfaces

by
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Kinetic studies of insecticide degradation gives important information on the half-life necessary to predict their persistence in the environment. The existent studies on Guthion (Azinphosmethyl: 0.0-dimethyl S - [4 - oxo - 1,2,3 - benzotriazin - 3 (4H) - ylmethyl] phosphorotioate) in water and glass surfaces were only static ones (Schultz et al., 1970; Liang and Lichtenstein, 1972), and consequently a prediction of the insecticide persistence is difficult to obtain from the available data.

This work was designed to calculate the half-life of Guthion in aqueous solutions and in glass beads as affected by pH and temperature.

Materials and Methods

In the experiment pure and radioactive Azinphosmethyl, labelled at the methylene carbon group, was used. Both products were synthesized in our laboratory from the commercially available methyl anthranilate with an overall yield of 33%. Intermediate and final products were identified by NMR spectroscopy and by comparison with reported physical data. The glass beads used in the experiment was < 60 mesh.

Guthion was extracted from water with chloroform in a ratio of 1:1. Preliminary tests showed that by this procedure a 100% recovery is obtained. The Guthion was determined by gas chromatography using a Packard Model G.C. with a flame photometric detector. The conditions for the GLC were: glass column 90 cm x 3 mm I.D. filled with 10% SE-30 on Gas Chrome Q 80-100 mesh. Inlet and column temperature 245°C, detector temperature 200°C, carrier gas flow 60-70 ml per min. Two µl of Azinphosmethyl solution at a concentration of 20 ppm in chloroform was injected as a standard after each two injections of samples. Peak height was used for quantitation. A Packard 3003 Tri Carb liquid scintillation spectrometer was used for counting ^{14}C activity. The scintilattion liquid consisted of: 60 g naphtalene, 4 g PPO (2,5 - diphenyloxazole), 0.2 g POPOP - 1,4 bis - 2 - (4 - methyl - 5 - phenyloxazolyl) benzene, 100 cc methyl alcohol and 20 cc ethylene glycol, brought to 1 liter with 1,4 - dioxan.

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Solutions of ^{14}C - Guthion in water were buffered at pH 8.6, 9.6 or 10.7 and placed at three temperatures: 6°C, 25°C, and 40°C. At different intervals up to 25 days, 5 ml of each sample was extracted with 5 ml of chloroform and analyzed. The organic phase was tested by gas chromatography. The ratio between degradable products and the persistent ^{14}C - Guthion was established by measuring the radioactive carbon content in both the water and chloroform extract. The polar degradation products were measured in aqueous solutions considering that the non-degradable Guthion was measured in the chloroform solutions. The partition coefficient of the Guthion itself was taken into account. Good agreement between the ^{14}C-Guthion measured by liquid scintillation counting and by gas chromatography was observed.

Since Liang and Lichtenstein (1972) have established that none of the degradation compounds was toxic to insects, in our study we followed only the kinetics of Guthion degradation.

Results and Discussion

By plotting the logarithm of Guthion concentration in water or in glass beads versus time, a linear relationship may be observed. This fact confirms that the Guthion degradation follows first order kinetics. The half-life of Guthion - considered as the time required for the one half of the initial material to be lost during the degradation process - was calculated from the following equation:

$$t_{1/2} = \frac{1}{k_1} \ln \left[\frac{G_o}{G_o/2} \right] \qquad (1)$$

where

G_o represents the initial concentration of Guthion and $k_1 = -2.303$ (slope). The slope is obtained from the first order kinetic equation by plotting log $(G_o - x)$ versus t, x being the amount of Guthion decomposed per unit volume at any time (t).

Degradation in aqueous solutions. Fig. 1 shows the normal degradation curves of Guthion in water at three different temperatures (6°C, 25°C, 40°C) when the pH of the solution increases from 8.6 to 10.7. Since Liang and Lichtenstein (1972) established that the degradation of Guthion occurs only in alkaline water, no treatments of lower pH were included in the present experiment. It may be observed that the degradation of Guthion clearly increased with the increase of pH and of the temperature. Using equation (1) the half life of Guthion in water with different pH and at different temperatures was calculated (Table 1). The $t_{1/2}$ is given in days.

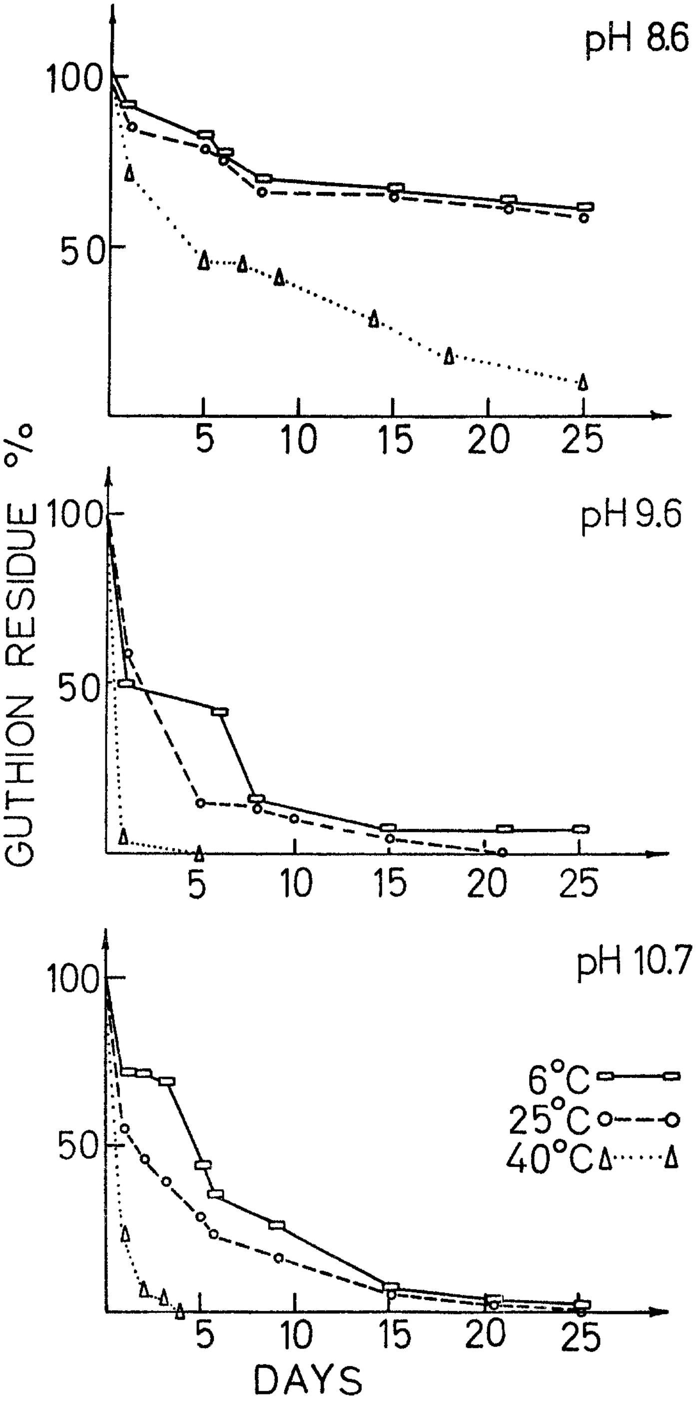


Fig. 1: Kinetics of Guthion degradation in aqueous solutions as affected by pH and temperature.

TABLE 1

The half-life ($t_{1/2}$) of Guthion in water as affected by pH and temperature (in days)

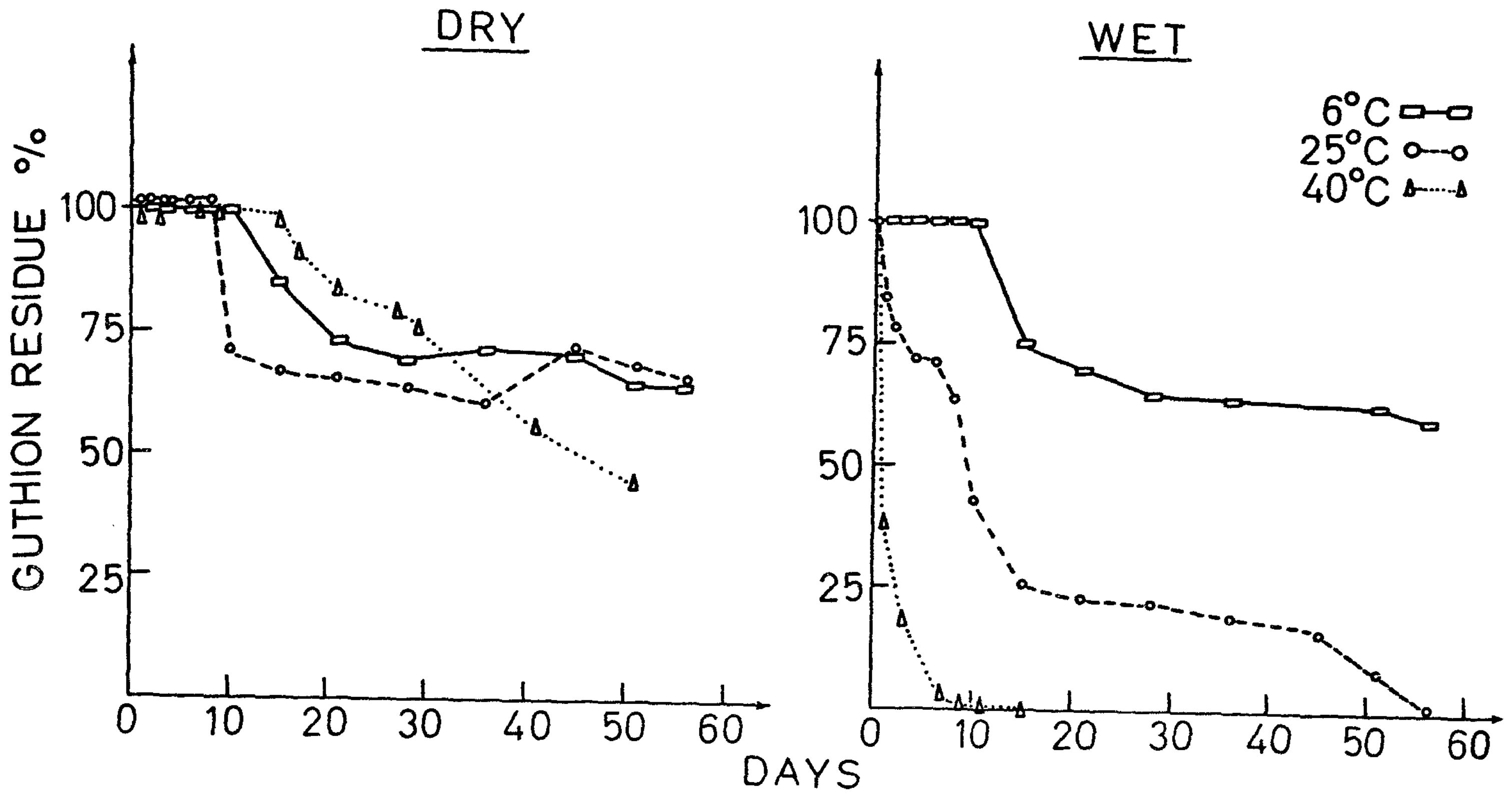
Temperature	pH 8.6		pH 9.6		pH 10.7	
	$t_{1/2}$	k_1	$t_{1/2}$	k_1	$t_{1/2}$	k_1
6°	36.4	$1.9x10^{-2}$	4.95	0.140	3.9	$1.8x10^{-1}$
25°	27.9	$2.5x10^{-2}$	2.40	0.246	2.0	$3.4x10^{-1}$
40°	7.2	$9.5x10^{-2}$	0.65	1.060	0.41	$16.9x10^{-1}$

At a pH < 9 the half-life of the Guthion in water is about one month for the temperatures of 6° and 25°C. When the pH increases at values greater than 9.5 for all the temperatures studied, the Guthion's half-life is less than one week and at 40°C temperature is even less than one day.

Degradation on glass beads. Fig. 2 shows the kinetics of Guthion degradation on glass beadssurfaces when the glass beads were kept either dry during the incubation period or when 1 cc of water was added to the glass beads. The pH of glass beads - water paste was 9.6, probably as a result of free Na released by the material. It may be observed that for all temperatures the Guthion is decomposed less on the dry glass beads than in the case with glass beads having a 50% moisture content. In the case of the air-dried glass beads a "lag period" is observed between the pesticide incubation and the beginning of the degradation process. This "lag period" was observed in soil (Yaron et al., 1973), where it decreased with the increase of the temperature and water content. Because the experiment was done on sterile glass beads, it is to be supposed that the "lag period" is not a biological effect; further studies have to clarify the understanding of this phenomenon. In the computing of the half-life, the "lag period" has to be considered. It was proposed to use the real half-life

$$T_{1/2} = t_o + t_{1/2} \qquad (2)$$

where t_o is the lag period between the application of pesticide and the start of the degradation process, and $t_{1/2}$ is as expressed in equation (1).



<u>Fig. 2</u>: Kinetics of Guthion degradation on glass beads surfaces.

TABLE 2

The half-life ($T_{1/2}$) of Guthion on glass beads as affected by moisture and temperature (in days).

Temperature	dry glass beads				wet glass beads			
	t_o	$t_{1/2}$	$T_{1/2}$	k_1	t_o	$t_{1/2}$	$T_{1/2}$	k_1
6°	10	89	99	7.8×10^{-3}	10	81	91	7.7×10^{-3}
25°	8	58	66	1.2×10^{-2}	0	10	10	6.1×10^{-2}
40°	9	39	48	1.8×10^{-2}	0	1	1	7.5×10^{-1}

Table 2 shows the half-life ($T_{1/2}$) of Guthion on glass beads as affected by water and temperature. It may be observed that in the presence of water the decomposition starts immediately after incubation at temperatures of 25°C and 40°C and the "lag period" is observed only at 6°C.

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