

除草活性を有する2-ジフルオロメチルチオ-4,6-ビス(イソプロピルアミノ)-1,3,5-トリアジンの光分解と加水分解

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Note

Photolysis and Hydrolysis of Herbicidal
2-Difluoromethylthio-4,6-bis(isopropyl-
amino)-1,3,5-triazine

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INTRODUCTION

SSH-108 [2-difluoromethylthio-4, 6-bis(isopropylamino)-1,3,5-triazine], prepared in our laboratory, is a new pre-emergence herbicide which effectively controls weeds in corn, soybean, wheat, cotton and other crops.¹⁾ In order to estimate the environmental fate of this compound, studies on its photolysis and hydrolysis were undertaken. Photolysis and hydrolysis are important factors when the spray deposit of a herbicide is lost in water, soil and plants. Numerous studies on the photolysis and hydrolysis of *s*-triazine have been reported.²⁻⁵⁾ The present study was aimed to examine the physicochemical effects of SSH-108 by observing its photolysis and hydrolysis in comparison with prometryn.

MATERIALS AND METHODS

1. *Chemicals*

SSH-108 was prepared by the method described in our previous paper¹⁾ and prometryn was synthesized according to the conventional method.⁶⁾ The purity of both compounds was over 98%.

2. *Photolysis by Artificial Light*

Filter papers (Toyo Roshi Co., No. 131, 70 mm diameter) were soaked in 0.25 ml of ethanol solutions containing either SSH-108 or prometryn at 1000 ppm. After air-drying at ambient temperature, the filter papers were placed in a covered transparent polyacryl plastic box (20 × 20 × 12 cm). The light of wavelength longer than 285 nm was then passed through the plastic cover. The box was exposed to artificial light from a 20 W fluorescent ultraviolet lamp

(FL-20SE, Toshiba, Japan), which emits UV light at wavelengths from 300 to 360 nm. The inside temperature of the irradiation apparatus was controlled with an electric fan to remain at 30°C. A dark control experiment was conducted under the same conditions, except that the filter papers soaked in either chemical solution were placed in an opaque vinylchloride box.

3. *Photolysis by Sunlight*

The filter papers prepared in the same manner as described above were placed in a transparent acrylic-resin box and directly exposed to sunlight from July 12 to 29, 1985. The temperature in the box was maintained in the range of 30 to 45°C during the day.

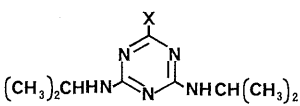
4. *Hydrolysis*

Hydrolysis of SSH-108 was carried out at pH 2, 4, 6, 8 and 10 ($\mu=0.2$) in Britton-Robinson buffer solution.⁷⁾ The buffer solution (1.5 ml) containing 20 $\mu\text{g/ml}$ of either SSH-108 or prometryn was put into 2 ml glass ampules. The ampules were sealed by flame and placed in a dark incubator maintained at $100 \pm 1^\circ\text{C}$. Progress in hydrolysis was monitored at regular time intervals.

5. *Analytical Procedure for Photolysis*

The filter papers treated with SSH-108 or prometryn were taken out from the apparatus after 30, 60 and 90 hr of irradiation and extracted with 25 ml of ethanol for 15 min. A ten-milliliter aliquot of each extract was diluted to 20 ml with ethanol containing an internal standard. SSH-108 or prometryn content in the ethanol solution was determined by HPLC equipped with a 6000A pump (Waters Associates), an ODS column (0.6 × 15 cm, Yamamura Chemicals, Japan), and UVIDEC-100 II detector with a fixed wavelength of 230 nm (JASCO, Japan). A methanol-water mixture (80:20) at a flow rate of 1.0 ml/min was used as the mobile phase. Benzophenone and 2,4,5-trichloronitrobenzene were used as the internal standards to prepare calibration curves for SSH-108 and prometryn, respectively. Retention times of SSH-108, prometryn, benzophenone and 2,4,5-trichloronitrobenzene were 7.9, 6.5, 6.0 and 8.5 min, respectively. Each average value was calculated from 2 replicates.

Table 1 Pseudo first-order rate constants (k) and corresponding half-lives ($T_{1/2}$) for SSH-108 and prometryn by photolysis under artificial light.



X = SCHF₂: SSH-108,
 X = SCH₃: Prometryn.

Compound	Recovery by HPLC (%) ^{a)} Time of photolysis (hr)			k (hr ⁻¹)	$T_{1/2}$ (hr)
	24	48	96		
SSH-108	89.3 (99.1) ^{b)}	63.6 (96.3)	33.5 (92.5)	1.07×10^{-2}	65
Prometryn	34.8 (95.0)	11.7 (92.3)	1.2 (92.2)	4.57×10^{-2}	15

^{a)} Average of duplicate experiments.

^{b)} Value in parentheses: dark control.

Table 2 Pseudo first-order rate constants (k) and corresponding half-lives ($T_{1/2}$) for SSH-108 and prometryn by photolysis under sunlight.

Compound	Recovery by HPLC (%) ^{a)} Time of photolysis (hr)			k (hr ⁻¹)	$T_{1/2}$ (hr)
	30	60	90		
SSH-108	63.8 (93.8) ^{b)}	45.8 (88.7)	30.1 (84.2)	1.33×10^{-2}	52
Prometryn	55.1 (99.3)	34.2 (98.2)	23.1 (97.8)	1.93×10^{-2}	36

^{a)} Average of duplicate experiments.

^{b)} Value in parentheses: dark control.

6. Analytical Procedure for Hydrolysis

At intervals of 2, 4 and 8 days, the sealed ampules were opened and 1 ml of the contents was diluted to 2 ml with ethanol containing the internal standard. SSH-108 or prometryn content was determined by HPLC as described above.

RESULTS AND DISCUSSION

The results of kinetic studies on the photolysis of SSH-108 and prometryn are shown in Tables 1 and 2. The rate constants (k) and half-lives ($T_{1/2}$) were calculated using Eqs. (1) and (2), respectively.

$$k = (\ln C_0 - \ln C) / t \quad (1)$$

$$T_{1/2} = (\ln 2) / k \quad (2)$$

where C_0 is an initial concentration of substrate and C is a concentration at time t . All of the decline curves were graphically linear as shown in Fig. 1, indicating the pseudo first-order reaction kinetics. The half-life values ($T_{1/2}$) of SSH-108 were 65 and 52 hr under artificial light and

sunlight, respectively. The above findings implied that SSH-108 was approximately 4.3 times and 1.4 times more stable than prometryn under artificial light and sunlight, respectively. Jordan *et al.*²⁾ summarized the photolysis of *s*-triazine. Zabik *et al.*³⁻⁵⁾ studied the photodegradation of halo-, methoxy-, methylthio- and hydroxy-*s*-triazines and suggested that the photolysis of 2-methylthio-*s*-triazines proceeds *via* concerted rearrangement involving an intramolecular hydrogen shift. The slower photolysis rate of SSH-108 compared with that of prometryn may be attributed to a decrease in electron density on the hydrogen atom of difluoromethyl substituent, because fluorine atoms withdraw electrons.

Hydrolysis experiments of SSH-108 and prometryn were carried out in buffer solutions at $100 \pm 1^\circ\text{C}$ in the pH range of 2 to 10. After 2, 4 and 8 days, the recovery of substrate was determined. Rate constants (k) and half-lives ($T_{1/2}$) were calculated in the same way as described above (Table 3). The results indicated that the rate constants (k) of SSH-108 were higher than

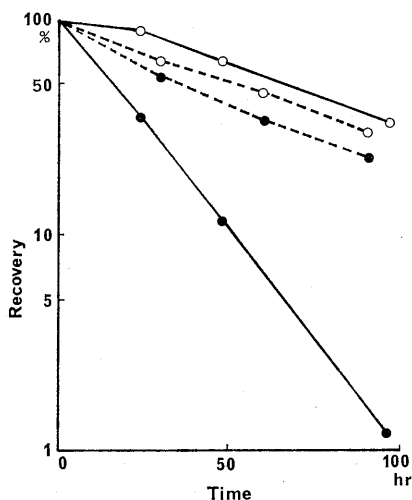


Fig. 1 Photolysis rates of SSH-108 (O) and prometryn (●) on filter paper under artificial light (—) and sunlight (---).

—O—: $\ln C = -0.013t + 4.80$ $r = 0.9999$, —●—: $\ln C = -0.047t + 4.69$ $r = 0.9999$, ---O---: $\ln C = -0.013t + 4.55$ $r = 0.9977$, ---●---: $\ln C = -0.015t + 4.43$ $r = 0.9984$.

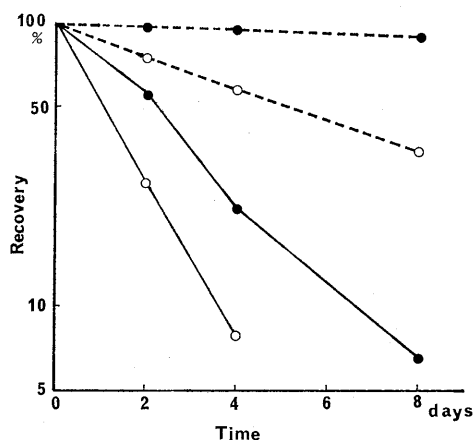


Fig. 2 Hydrolysis rates of SSH-108 (O) and prometryn (●).

—: pH 2, ---: pH 10. —O—: $\ln C = -0.631t + 4.57$ $r = 0.9998$, —●—: $\ln C = -0.352t + 4.65$ $r = 0.9984$, ---O---: $\ln C = -0.135t + 4.61$ $r = 0.9972$, ---●---: $\ln C = -0.016t + 4.60$ $r = 0.9722$.

Table 3 Pseudo first-order rate constants (k) and corresponding half-lives ($T_{1/2}$) for SSH-108 and prometryn by hydrolysis at 100°C in the range from pH 2 to 10.

Compound	pH	Recovery by HPLC (%) ^{a)} Time of hydrolysis (day)			k (day ⁻¹)	$T_{1/2}$ (day)
		2	4	8		
SSH-108	2	26.7	7.8	— ^{b)}	6.4×10^{-1}	1
	4	91.8	87.7	78.5	3.1×10^{-2}	22
	6	98.0	97.2	95.5	6.3×10^{-3}	111
	8	95.5	91.5	87.5	1.8×10^{-2}	39
	10	74.2	57.3	34.6	1.3×10^{-1}	5
Prometryn	2	55.6	23.9	6.4	3.5×10^{-1}	2
	4	95.9	93.7	90.6	1.3×10^{-2}	52
	6	97.2	96.3	93.5	8.9×10^{-3}	78
	8	108.0	95.2	93.9	8.7×10^{-3}	80
	10	96.0	92.3	88.6	1.6×10^{-2}	43

^{a)} Average of duplicate experiments.

^{b)} Data not available.

those of prometryn, particularly at pH 10. Typical plots for acidic (pH 2) and basic (pH 10) solutions are shown in Fig. 2. In all experiments, hydrolysis proceeded by pseudo first-order kinetics. The more rapid hydrolysis of SSH-108 could be attributed to the effect of the difluoromethylthio group, which withdraws electrons from the triazine ring. Chemical hydrolysis of

s-triazines has been studied by many researchers.⁸⁻¹¹ It was found that *s*-triazine herbicides are detoxified by hydrolysis to non-phytotoxic hydroxy analogs.¹² The carbon atom bonded to the difluoromethylthio group on the ring is strongly electro-deficient and susceptible to displacement by strong nucleophilic agents such as hydroxide ions. On the other hand, weak

nucleophilic agents, such as water in the neutral pH region, have difficulty replacing the difluoromethylthio group. In the acidic pH region, hydrolysis rates of SSH-108 and prometryn were not remarkably different, because protonation of the nitrogen atom is a determining factor in hydrolysis. The nitrogen atom is far from methylthio or difluoromethylthio substituent and is similar in electron density.

SSH-108 was different from prometryn in behavior: it was more stable to photolysis on filter paper and less stable to hydrolysis, except at pH 6. Although the conditions employed in this experiment were not the same as in the natural environment, the results obtained could serve to clarify the behavior of SSH-108 in the natural environment.

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要 約

除草活性を有する 2-ジフルオロメチルチオ-4,6-ビス(イソプロピルアミノ)-1,3,5-トリアジンの光分解と加水分解

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2-Difluoromethylthio-4,6-bis(isopropylamino)-1,3,5-triazine (SSH-108) の人工光と太陽光による分解を検討した。SSH-108 とプロメトリンをろ紙上で人工光に照射した場合の半減期は、SSH-108 で 65 時間、プロメトリンで 15 時間であった。一方、太陽光の場合では SSH-108 が 52 時間、プロメトリン 36 時間の半減期であり、光分解に関し SSH-108 はプロメトリンより安定であった。pH 2~10 の buffer 中 100°C で、SSH-108 とプロメトリンの加水分解性を比較した。pH 6 以外の酸性、塩基性領域では、SSH-108 はプロメトリンより分解が速く、とくに pH 10 ではプロメトリンの半減期が 43 時間であったのに対し、SSH-108 は 5 時間であった。