

# PHOTOLYTIC DEGRADATION OF CHLOROTHALONIL IN DIFFERENT ORGANIC SOLVENTS UNDER NATURAL SUNLIGHT IRRADIATION

Zhang LF\*, Niu S, Dong L, Yang WL, Zhang T, Shi SX, Zhou L, Zhang XL, Li LL, Wu ZX, Huang YR

State Environmental Protection Key Laboratory of Dioxin Pollution Control, National Research Center for Environmental Analysis and Measurement, No. 1 Yuhui Nanlu, Chaoyang District, Beijing 100029, China (\*corresponding author: Dr. Lifei Zhang, Email: lfzhang@cneac.com)

## Introduction

Chlorothalonil (2,4,5,6-tetrachloroisophthalonitrile) is a broad spectrum, contact, or protectant fungicide with long residual activity. It is one of the most commonly used organochlorine fungicides worldwide. In 2001, chlorothalonil ranked 13th in pesticide usage in the USA<sup>1</sup>. Chlorothalonil production enterprises were mainly distributed in Jiangsu, Shandong, and Hunan provinces in China. The annual production of chlorothalonil was more than 10,000 tons in China in 2007<sup>2</sup>.

Several studies have been published on the degradation of chlorothalonil in various matrix, like water<sup>3</sup>, soil<sup>4,5</sup>, and plant leaf<sup>1</sup>. However, few studies have focused on the photodegradation of chlorothalonil in organic solvents used in the lab. In this paper, we aimed at estimating and rationalizing chlorothalonil photodegradation in acetone, hexane and several other organic solvents commonly used in the chemical laboratory.

## Materials and methods

Organic solvents including hexane, ethyl acetate (EtAc), dichloromethane (DCM), acetone, acetonitrile (ACN), and methanol (MeOH) for organic residue analysis were purchased from J.T. Baker, USA. Chlorothalonil standard solution (1000 mg/L, in acetone) was from Agro-environmental Protection Institute, Ministry of Agriculture, Tianjin, China. <sup>13</sup>C-hexachlorobenzene was purchased from Wako, Japan.

Chlorothalonil and <sup>13</sup>C-hexachlorobenzene standard mixtures (with concentrations 10 µg/mL each, volume 1.0 mL) were prepared with different organic solvents in transparent glass vials for degradation experiment under natural sunlight for variable days.

The determination of chlorothalonil was performed on a GC-MS (2010plus, Shimadzu, Japan) equipped with a fused silica capillary DB-5ms (30m × 0.25 mm i.d., film thickness 0.25 µm, Agilent, USA) column using electron ionization with scan mode. High purity helium was used as the carrier gas at 1.0 mL/min. The injection, interface, and ion source temperatures were 260, 300 and 230°C, respectively. The oven temperature program was as follows: initial temperature 50°C, held for 0.5min; increased to 200°C at 5°C/min, held for 4.5 min. The scan m/z ranged from 45 to 300. Two microliters of each sample was injected in splitless mode.

## Results and discussion

### 1. Chlorothalonil degradation in different organic solvents

<sup>13</sup>C-hexachlorobenzene was used as a reference compound in this study. The abundance of chlorothalonil compared to <sup>13</sup>C-hexachlorobenzene in different solvents after sunlight irradiation are shown in Fig. 1. For MS detector, chlorothalonil in ACN has the highest response, almost two times higher than DCM and acetone.

The chlorothalonil absorption spectrum in organic solvents overlaps with solar radiation spectrum. Therefore, it is susceptible to direct photolysis<sup>1</sup>. Chlorothalonil could be completely degraded in different organic solvents under natural sunlight irradiation after 77 days. However, chlorothalonil was relatively more stable in EtAc and hexane than in other organic solvents when exposed to sunlight. Chlorothalonil can be entirely decomposed after 9 days when it was stored in DCM, acetone, ACN, or MeOH.

The photolytic degradation kinetic of chlorothalonil in different organic solvents are given in Table 1. The calculation of half-life was performed using the first-order rate equation:  $C_t = C_0 e^{-kt}$ .

Where  $C_t$  represents the concentration at time  $t$ ;  $C_0$  represents the initial concentration and  $k$  is the rate constant.

When the concentration is reduced to 50% of its initial amount, the half-life ( $t_{1/2}$ ) can be determined by:

$t_{1/2} = 0.693/k$ . Where  $k$  is the degradation constant.

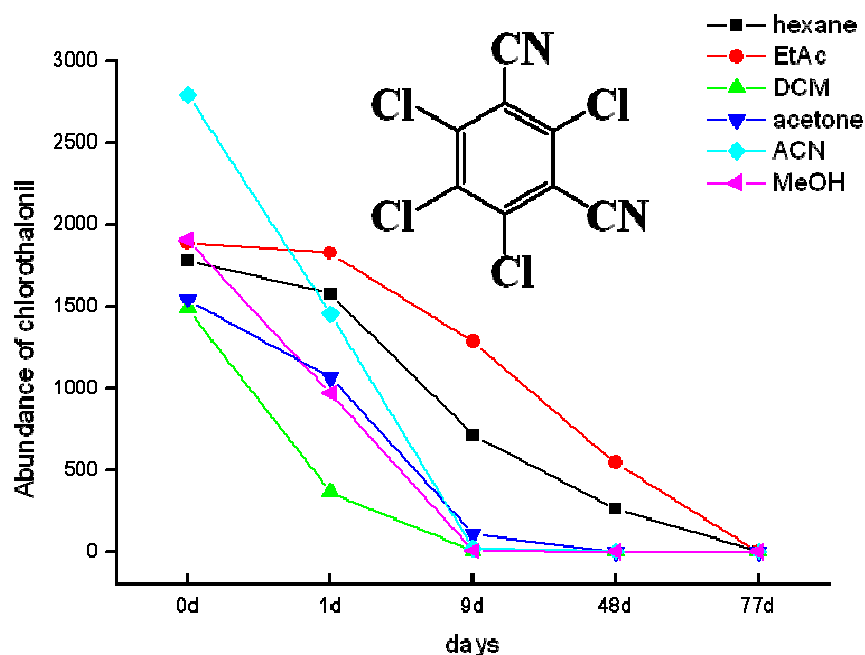


Fig. 1 Abundance of chlorothalonil in different solvents after sunlight irradiation

All photodegradation reactions determined in this work were of first order with  $R^2$  ranged from 0.913 to 0.999. As shown in Table 1, the half-lives of the photo degradation of chlorothalonil were 18.7 and 27.7 days in hexane and EtAc, respectively. The half-lives in DCM, acetone, ACN, and MeOH were less than 2.5 days. However, these values were higher than it in water, which just few hours<sup>3</sup>. Chlorothalonil has the ability to produce singlet oxygen very efficiently (near 100%). Hydroxylated chlorothalonil was proposed to be formed by a photoassisted nucleophilic substitution, but it was never detected due to the high degradation rate<sup>6</sup>. Furthermore, the existence of MeOH, DCM, and ACN etc. polar organic solvents can accelerate this process. Unfortunately, statistical results (Pearson correlation analysis) indicated that there are no significant ( $P$  values ranged from 0.223 to 0.977) correlation between half-life and solvents' phys-chemical properties, such as dielectric constant, viscosity, or boiling point.

Table 1 Photodegradation kinetic of chlorothalonil in different organic solvents

solvent	exponential equation	$R^2$	$t_{1/2}$ (days)
hexane	$y=1461.0e^{-0.037x}$	0.913	18.7
EtAc	$y=1795.8e^{-0.025x}$	0.984	27.7
DCM	$y=1041.5e^{-0.649x}$	0.986	1.1
acetone	$y=1484.8e^{-0.289x}$	0.999	2.4
ACN	$y=2645.6e^{-0.537x}$	0.999	1.3
MeOH	$y=1862.3e^{-0.628x}$	0.999	1.1

## 2. Transformation of degradation products

Previous studies show that the chemical transformation of chlorothalonil is not due to reaction with oxygen<sup>1</sup>. Photoproduct identification by Monadjemi et al.<sup>1</sup> showed that the main reaction path for chlorothalonil in *n*-heptane was a reductive dehalogenation. Direct irradiation will lead to the promotion of the pesticides to their excited singlet states, which may then intersystem cross to produce triplet states<sup>7</sup>. Such excited states can then undergo the radical (H donor) mechanism. In this study, it's worth mentioning that pentachlorobenzonitrile

(retention time (RT): 28.23 min) as the impurity of chlorothalonil was detected in the beginning day. In addition, two tetrachlorophthalonitriles (RT: 29.09 min and 28.71 min) were also detected during the first nine days. But these compounds were ignored due to their low abundances.

Fig. 2 shows the variation of four chlorothalonil photodegradation products detected in different organic solvents. There are three possible isomers of trichloro-1,3-dicyanobenzene (M1), but only two (RT: 26.56 min and 25.97 min) were detected in the current study. Accordingly, two (RT: 22.80 min and 22.20 min) dichloro-1,3-dicyanobenzene (M2) and two (RT: 18.37 min and 17.99 min) chloro-1,3-dicyanobenzene (M3) were found in the degradation products. Moreover, 2,5,6-trichloro-4-methoxy isophthalonitrile (M4, RT: 29.89 min) was also detected in the degradation products.

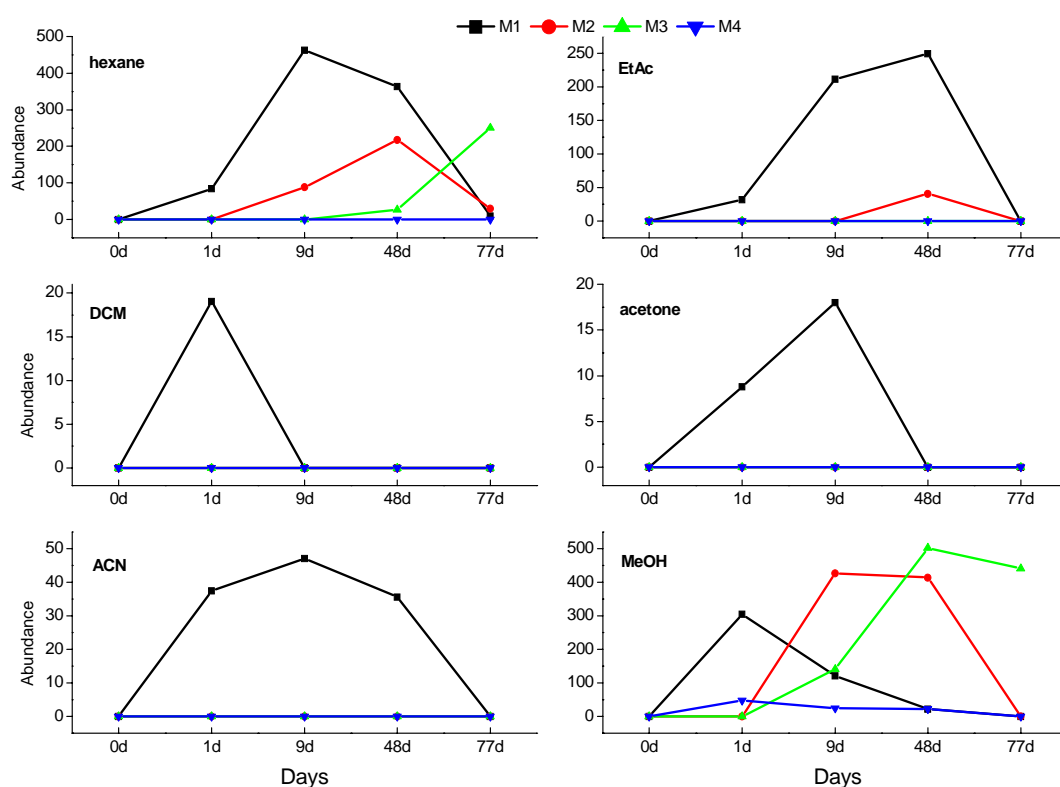


Fig. 2 Variation on chlorothalonil photodegradation products in different organic solvents (M1: trichloro-1,3-dicyanobenzene; M2: dichloro-1,3-dicyanobenzene; M3: chloro-1,3-dicyanobenzene; M4: 2,5,6-trichloro-4-methoxy isophthalonitrile)

M1 was produced in all of the organic solvents at the beginning days, and it was died away after 77 days. M2 was generated in hexane, EtAc, and MeOH, it was also decreased to zero after 77 days. M3 was produced only in hexane and MeOH, and it increased with the reaction time. M4 was only detected in MeOH after one day reaction. Based on these findings, it could be concluded that reductive dehalogenation was the main route for chlorothalonil photodegradation. The homolytic cleavage of the C-Cl bond may occur in hexane. At the same time, the presence of M4 in MeOH confirms that the reaction may be initiated by an electron transfer by a H donor molecule, followed by a proton transfer to form two radicals. Homolytic and radical mechanism were coexist during the photodegradation of chlorothalonil in different organic solvents under natural sunlight irradiation.

### Acknowledgements

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### References

1. Monadjemi S, El Roz M, Richard C, Ter Halle A. (2011); *Environ. Sci. Technol.* 45(22): 9582-9
2. Du YP (2007). *Research on limit value of chlorothalonil discharge standards*. Master Thesis
3. Penuela GA, Barcelo D. (1998); *J. Chromatogr. A* 823(1-2): 81-90
4. Regitano JB, Tornisielo VL, Lavorenti A, Pacovsky RS. (2001); *Arch. Environ. Contam. Toxicol.* 40(3): 295-302
5. Hladik ML, Kuivila KM. (2008); *J. Agric. Food Chem.* 56(7): 2310-4
6. Kwon JW, Armbrust KL. (2006); *J. Agric. Food Chem.* 54(10): 3651-7
7. Burrows HD, Canle LM, Santaballa JA, Steenken S. (2002); *J. Photoch. Photobio. B* 67(2): 71-108