

# ISIRR 2003

## DIRECT PHOTOLYSIS OF 2-AMINO-5-CHLOROPYRIDINE

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### **Abstract:**

*Kinetics of direct photolysis of a pyridine pesticide analogue, 2-amino-5-chloropyridine, have been investigated at different initial concentrations of the substrate. Kinetics were studied by monitoring the reaction of chloride generation by direct potentiometry. Upon comparing the reaction of direct photolysis with the reaction in the presence of  $TiO_2$  it was found that the reaction of chloride elimination, i.e. degradation of the initial substrate takes place at a greater rate in case of direct photolysis than it does in the presence of  $TiO_2$ .*

### **Keywords:**

*direct photolysis,  $TiO_2$ , 2-amino-5-chloropyridine, water remediation*

## 1. INTRODUCTION

Contamination of waterstreams by different organic pollutants is becoming an increasing environmental problem. Because water supplies are limited in the world, there is a need for development of new methods for water remediation. These methods should be efficient and cost-effective. There have been attempts to apply the direct photolysis process to these purposes [2,3,5,7-12]. The direct photolytic process is based on the use of UV-light for degradation of organic compounds. In many cases, direct photolysis is not an efficient process regarding complete mineralization, but causes degradation of organic compounds to some extent. Heterogeneous photocatalysis, on the other hand, has proven to be an efficient method to completely mineralize organic compounds [1,4,6,10,12,14,15]. For this reason, the aim of this work was to investigate the kinetics of direct photolysis of a pyridine pesticide analogue [13], 2-amino-5-chloropyridine, at different initial concentrations of the substrate and compare them to the kinetics of photocatalytic degradation. Potentiometric monitoring of chloride generated during the process was used for these purposes.

## 2. EXPERIMENTAL

### *Reagents and solutions*

All chemicals used were of reagent grade. 2-amino-5-chloropyridine, as well as  $\text{KNO}_3$ , were purchased from Merck. NaCl was purchased from Zorka (Šabac, Serbia and Montenegro). Titanium dioxide Degussa P25 (specific surface area  $50 \pm 15 \text{ m}^2/\text{g}$ , nonporous) was used as photocatalyst. In all experiments doubly-distilled water was used.

For the investigation of the effect of initial substrate concentration, a stock solution of 2-amino-5-chloropyridine ( $c \sim 2.5 \text{ mmol}/\text{dm}^3$ ) was prepared. This solution was appropriately diluted to obtain solutions of lower concentrations ( $0.5 - 2.0 \text{ mmol}/\text{dm}^3$ ).

For calibration of the chloride electrode, a stock solution of NaCl ( $100 \text{ mmol}/\text{dm}^3$ ) was prepared. By multiple dilution of this solution, a series of standards was prepared ( $0.01 - 3 \text{ mmol}/\text{dm}^3$ ). Since titanium dioxide contains chlorides, by manufacturers declaration, it was added to the standard solutions in the same amount ( $2 \text{ mg}/\text{cm}^3$ ) as for the photodegradation procedure.

### *Photodegradation procedure*

For the experiments  $20.0 \text{ cm}^3$  of the investigated compound solution were measured into a double-walled photochemical cell made of Pyrex glass, equipped with a magnetic stirring bar.  $\text{KNO}_3$  ( $100 \text{ mmol}/\text{dm}^3$ ) was then added to keep the ionic strength constant during irradiation. For the photocatalytic degradation experiments, 40 mg of titanium dioxide were added and the solution was sonified to make the particles uniform. Thus obtained solution was then thermostated at  $40 \pm 0.5 \text{ }^\circ\text{C}$  in a stream of oxygen. A 125 W Philips HPL-N mercury lamp, with the highest emitted intensity in the UV region at 365 nm, was used as the irradiation source.

### *Analytical procedure*

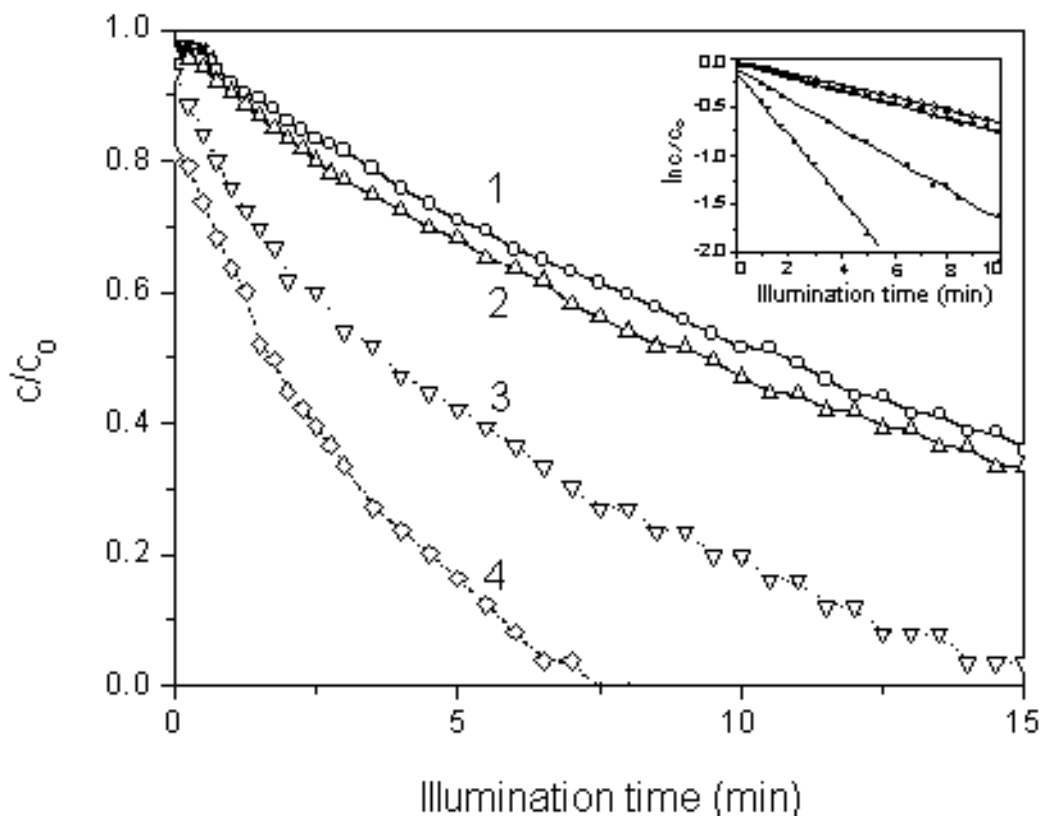
Concentration changes of chloride generated during the degradation were monitored by a chloride ion selective electrode (Mettler Toledo Me-51340400) coupled to a saturated calomel electrode (Iskra K401) via a potassium nitrate electrolytic bridge and connected to a pH-meter (Radiometer PHM62).

## 3. RESULTS AND DISCUSSION

Since photocatalytic degradation is in most cases a more efficient method for degradation of organic compounds than direct photolysis [1,3,8,12], the efficiency of photocatalytic degradation of 2-amino-5-chloropyridine was primarily investigated. Kinetics of the degradation were monitored by determination of chloride generated in the reaction, since these two processes take place simultaneously.

Upon investigation of the degradation of the substrate in presence of titanium dioxide (Fig. 1), it was found that the reaction is of the first-order, in the entire investigated concentration range. However, the values for the reaction rate constants (Table 1) were significantly higher than those found in literature [1,4,6,8,15]. According to the mechanism which involves the reaction with hydroxyl radicals formed by excitation of  $\text{TiO}_2$ , these values should be independent from the compound type [16]. This discrepancy indicates that the reaction of chloride elimination takes

place by another mechanism – one not involving the hydroxyl radicals formed on the surface of titanium dioxide. It can also be concluded from Table 1 that the decrease in the reaction rate constant is more pronounced at lower concentrations.



**Fig. 1.** The effect of the initial concentration of 2-amino-5-chloropyridine ( $\text{mmol/dm}^3$ ) on the rate of photodegradation in the presence of  $\text{TiO}_2$  ( $2 \text{ mg/cm}^3$ ): (1) 2.5; (2) 2.0; (3) 1.0; (4) 0.5. The insert represents the linear transform  $\ln(c/c_0) = f(\text{illumination time})$ .

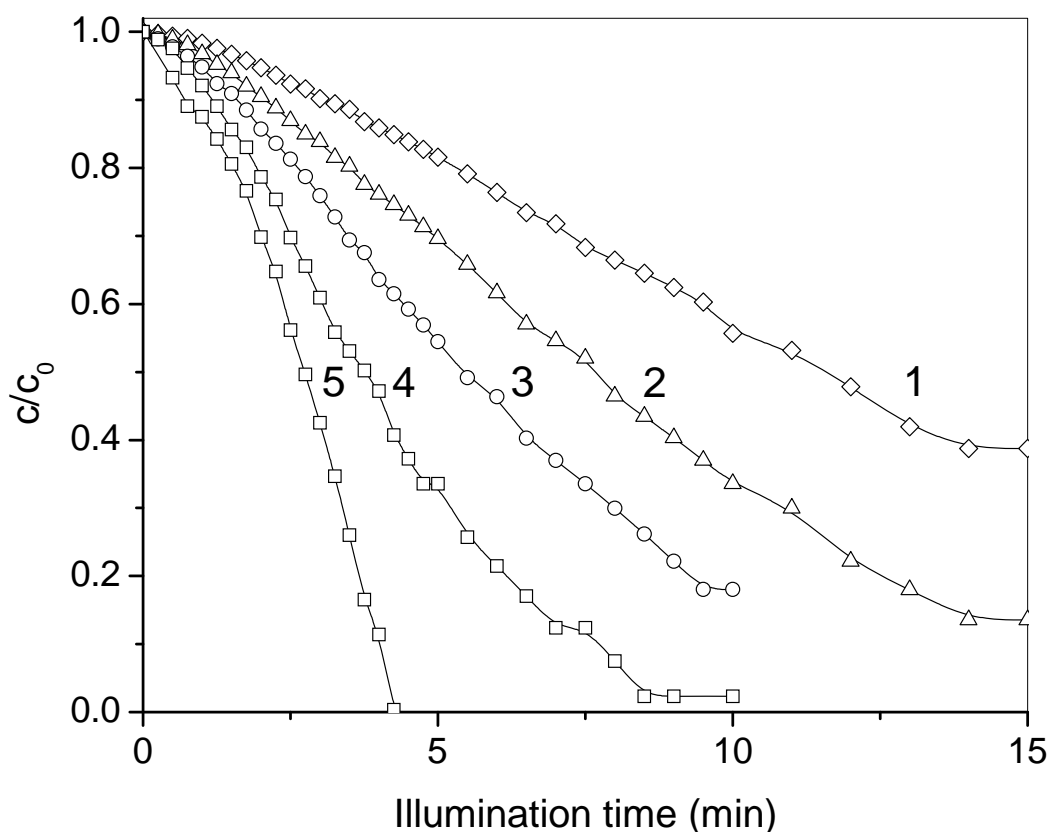
**Table 1.** Effect of initial concentration ( $c_0$ ) of 2-amino-5-chloropyridine on the rate of photodegradation in the presence of  $\text{TiO}_2$  ( $2 \text{ mg/cm}^3$ )

| $c_0$ ( $\text{mmol/dm}^3$ ) | $10^2 k$ ( $\text{min}^{-1}$ ) <sup>§</sup> | $r^\dagger$ | $t_{1/2}$ (min) <sup>‡</sup> |
|------------------------------|---|-------------|------------------------------|
| 0.5                          | 34  | 0.998       | 2.0                          |
| 1.0                          | 15  | 0.999       | 3.8                          |
| 2.0                          | 7.1   | 0.999       | 9.3                          |
| 2.5                          | 6.3   | 0.999       | 10.7                         |

<sup>§</sup>first-order rate constant; <sup>†</sup> linear regression coefficient; <sup>‡</sup> half-life.

For this reason kinetics of photodegradation were studied in the absence of titanium dioxide, i.e. under the conditions of direct photolysis. The effect of the initial substrate concentration is presented in Fig. 2. It was found that not only does the reaction take place in the absence of titanium dioxide, but it is somewhat faster and

of the zero-order (Table 2), which further supports the fact that the reaction doesn't take place via hydroxyl radical mechanism generated from  $\text{TiO}_2$ , but by another mechanism. Namely, although the half-lives of the reactions are similar, the time necessary for chloride elimination is mainly lower. Lower reaction rate of chloride elimination in the presence of titanium dioxide is probably a consequence of the opacity of the suspension and light scattering by titanium dioxide particles.



**Fig. 2.** Effect of initial concentrations of 2-amino-5-chloropyridine ( $\text{mmol/dm}^3$ ) on the rate of direct photolysis: (1) 2.5 ; (2) 2.0; (3) 1.5; (4) 1.0; (5) 0.5.

**Table 2.** Effect of initial concentration ( $c_0$ ) of 2-amino-5-chloropyridine on the rate of direct photolysis

| $c_0$ ( $\text{mmol/dm}^3$ ) | $10^4 k$ ( $\text{mol dm}^{-3} \text{min}^{-1}$ ) <sup>§</sup> | $r^\dagger$ | $t_{1/2}$ (min) <sup>‡</sup> |
|------------------------------|--|-------------|------------------------------|
| 0.5                          | 1.0  | 0.991       | 2.6                          |
| 1.0                          | 1.3  | 0.998       | 3.8                          |
| 1.5                          | 1.3  | 0.999       | 5.8                          |
| 2.0                          | 1.3  | 0.999       | 7.8                          |
| 2.5                          | 1.1  | 0.999       | 11.7                         |

<sup>§</sup> zero-order rate constant; <sup>†</sup> linear regression coefficient; <sup>‡</sup> half-life.

As can be seen from Table 2, in the case of the reaction of direct photolysis, the reaction rate constants have similar values as expected, which as was discussed, is not the case with photodegradation in the presence of TiO<sub>2</sub>.

#### 4. CONCLUSION

During the investigation of direct photolysis of 2-amino-5-chloropyridine it was found that its dechlorination is a fast process, in the entire investigated concentration range, as well as that it follows zero-order kinetics. Kinetics of chloride evolution for direct photolysis and photodegradation in the presence of TiO<sub>2</sub> were compared. It was found that the reaction of chloride evolution is retarded by TiO<sub>2</sub> presence due to the opacity of the suspension and light scattering by its particles. However, high rate of the initial compound degradation doesn't necessarily indicate its complete mineralization. Namely, formation of much more stable, and what's probably worse more toxic intermediates is very common.

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**Acknowledgement:**

*The work is financed by the Ministry of Science, Technology and Development of the Republic of Serbia (Project: "Development of New and Improvement of the Existing Analytical Methods and Techniques for Monitoring Quality of the Environment", No 1622).*