

Direct photolysis and photocatalytic degradation of 2-amino-5-chloropyridine

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Abstract: The direct photolysis and photocatalytic degradation of a pyridine pesticide analogue, 2-amino-5-chloropyridine, were investigated employing different analytical techniques – potentiometry, for monitoring the pH and chloride generation, spectrophotometry, for studying the degradation of the pyridine moiety, ion chromatography, for monitoring nitrate formation, and total organic carbon analysis for investigating the efficiency of the process. The photocatalytic degradation was studied in aqueous suspensions of titanium dioxide under illumination by UV light. It was found that chloride evolution was a zero-order reaction which takes place by direct photolysis, in that way differing from the degradation of the pyridine moiety, which takes place in the presence of titanium dioxide. Changes in pH during degradation indicate the formation of acidic intermediates and nitrate in addition to chloride. The effect of the initial substrate concentration was also investigated by monitoring the reaction of chloride generation as well as the degradation reaction of the pyridine moiety. It was found that degradation of the parent compound (2.5 mmol/dm³) by direct photolysis is completed in about 20 minutes, and of the pyridine moiety by photocatalytic degradation in about nine hours. Based on the obtained data a possible reaction mechanism is proposed.

Keywords: direct photolysis, photocatalytic degradation, titanium dioxide, 2-amino-5-chloropyridine, water treatment.

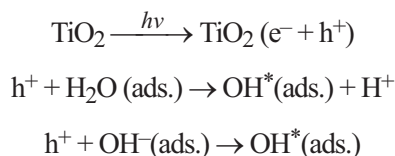
INTRODUCTION

Pollution of waterstreams by different organic pollutants, among which pesticides are very common, represents a serious environmental problem. Several conventional methods of water treatment exist, and as such have found certain practical applications. They are, however, either slow or non-destructive for some more persistent organic pollutants. On the contrary, heterogeneous photocatalysis with titanium dioxide as catalyst under UV irradiation was proven to be an efficient method to completely mineralise organic compounds.^{1–12} Namely, during this

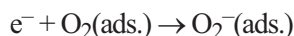
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process, organic carbon and hydrogen are transformed to carbon dioxide and water, while covalently bound halogen, nitrogen, sulphur and phosphorus are transformed to halide, ammonium/nitrite/nitrate, sulphate and phosphate, respectively. It is also important to point out that the inertness, low toxicity and low cost of titanium dioxide make it a good choice of semi conductor for heterogeneous photocatalysis.

When TiO₂ is illuminated with UV radiation, electron-hole pairs are formed.¹³ The thus generated holes are strong oxidizing agents ($E = +2.8$ V). In the reaction between the photogenerated holes and the water molecules and hydroxyl ions adsorbed on the TiO₂ surface, hydroxyl radicals capable of the mineralization of organic compounds are formed:



To prevent electron-hole recombination, it is necessary for the illumination to take place in the presence of an electron acceptor. For this purpose, illumination is most often carried out in an oxygen stream:



In this work, the photocatalytic degradation of an analogue of pyridine pesticides,¹⁴ 2-amino-5-chloropyridine, was studied by potentiometry, spectrophotometry, ion chromatography and by monitoring the change in the content of total organic carbon (TOC) in order to gain insight into the reaction kinetics and the nature of the intermediates involved and, consequently, to propose the probable mechanism of 2-amino-5-chloropyridine photodegradation. The effect of the initial concentration was also investigated.

EXPERIMENTAL

Chemicals and solutions

All chemicals used in the investigation were reagent grade and were used without further purification. 2-Amino-5-chloropyridine was purchased from Merck. The titanium dioxide used as photocatalyst was Degussa P25 (predominantly anatase, 50 m²/g, nonporous). The solutions were prepared with doubly distilled water. Milli-Q water was used as a component of the mobile phase in the ion chromatography.

For the investigation of the effect of the initial concentration of 2-amino-5-chloropyridine, stock solutions (2.5 and 2.9 mmol/dm³) were prepared. These solutions were diluted to prepare solutions of lower concentrations for investigation.

Standard chloride solutions for calibration were prepared by dilution of stock sodium chloride solution (100 mmol/dm³) to obtain solutions in the concentration range 0.01 – 3 mmol/dm³.

Photodegradation procedure

For the irradiation experiments, 20.0 cm³ of the to be investigated compound solution were measured into a double-walled photochemical cell made of Pyrex glass, equipped with a magnetic stirring bar. Then 40 mg of titanium dioxide were added, the solution was sonicated to make the par-

ticles uniform and then thermostated at 40 ± 0.5 °C in a stream of oxygen. A 125 W Philips HPL-N mercury lamp with the highest emitted intensity in the UV region at 366 nm, was used as the irradiation source.

Analytical procedure

The changes in the concentration of chloride generated during the degradation were monitored using 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). KNO_3 (100 mmol/dm^3) was added to maintain the ionic strength during irradiation constant.

Changes in the pH during the degradation were monitored by continuous potentiometry using a combined glass electrode (Iskra) connected to a recorder (Goerz Electro, type Servogor SbRE 647.9) *via* a pH-meter (Iskra MA 5706).

For spectrophotometric determinations during the degradation of the substrate in the presence of TiO_2 , as well as for direct photolysis experiments, aliquots of 0.2 cm^3 of the reaction mixture were taken at regular time intervals and diluted to 10.00 cm^3 . The solutions containing TiO_2 were filtered through membrane filters (Millex-GV, $0.22 \mu\text{m}$) to separate the TiO_2 particles before their spectra were recorded in the wavelength range from 200 to 400 nm using a Secomam Anthelie Advanced 2 spectrophotometer. The kinetics of the degradation were monitored at 239 nm.

For ion chromatographic determinations, aliquots of 0.25 cm^3 of the reaction mixture were taken at regular time intervals and diluted to 10.00 cm^3 . After dilution, these solutions were filtered in the same manner as for the spectrophotometric measurements, and analysed on an ion chromatograph Dionex DX-120 equipped with a Dionex AS14 column and a conductometric detector. The eluent was a mixture of Na_2CO_3 (3.5 mmol/dm^3) and NaHCO_3 (1 mmol/dm^3), flow rate $1.23 \text{ cm}^3/\text{min}$. For TOC analysis, samples were irradiated for different time intervals and analysed using a Euroglass TOC 1200 analyzer.

RESULTS AND DISCUSSION

The rate of 2-amino-5-chloropyridine degradation was monitored by measuring the rate of chloride formation because these two processes take place simultaneously. Since our results and the declaration of the manufacturer indicated the presence of chloride in the catalyst, for the calibration of the chloride electrode, titanium dioxide was added to the standard chloride solutions in the same amount as employed for the irradiation experiments.

The effect of the initial concentration of the substrate on the rate of chloride generation, as well as on the rate of substrate disappearance in the presence of titanium dioxide is presented in Fig. 1A. On the basis of these kinetic curves, a linear dependence of $\ln c/c_0$ on illumination time was obtained for heterogeneous photocatalysis for all the investigated initial concentrations (insert in Fig. 1A). This suggests that over the entire investigated concentration range, the degradation reaction of the substrate is first-order. The calculated values for the rate constant (k) are presented in Table I, together with the correlation coefficients for each of the fitted lines, and the corresponding half-life values. As can be seen, the values obtained for the rate constant are significantly higher than those found in literature, which they should be according to a mechanism involving hydroxyl radicals in the presence of titanium dioxide, independent of the type of the compound.¹³ This would suggest that the reaction of chloride generation, *i.e.*, degradation of the initial compound, is not

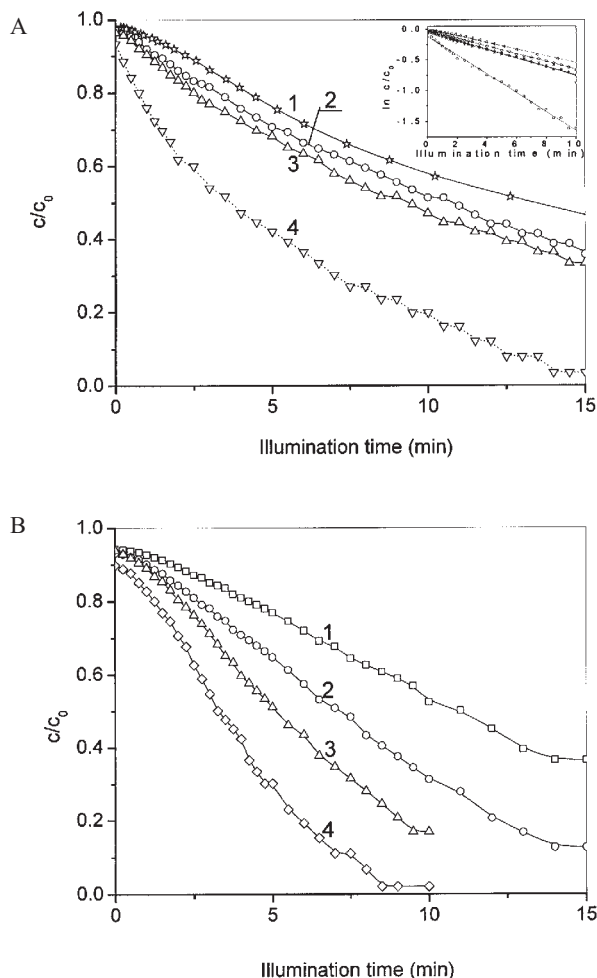


Fig. 1. Effect of the initial concentration of 2-amino-5-chloropyridine on its degradation rate monitored by potentiometry (mmol/dm^3): (A) (1) 2.9; (2) 2.5; (3) 2.0; (4) 1.0; in the presence of TiO_2 (2 mg/cm^3); (B) (1) 2.5; (2) 2.0; (3) 1.5; (4) 1.0; in the reaction of direct photolysis.

governed by hydroxyl radical formation on titanium dioxide, but that it takes place by another mechanism. For this reason the effect of the initial substrate concentration on the kinetics of chloride generation by direct photolysis was also investigated (Fig. 1B). It was found that the reaction of chlorine elimination not only occurs in the absence of titanium dioxide, but that it is faster and of zero-order (Table II), further supporting the assumption that the reaction takes place *via* a different mechanism. In this case, the opacity and light scattering by the titanium dioxide slurry diminishes the intensity of UV light, which explains the lower values for the rate of chloride generation in the presence of titanium dioxide. This effect becomes more evident with increasing initial substrate concentration and can be explained by the fact that there are more substrate molecules at higher concentrations resulting in a lower photon efficiency.

The results represented in Table I also show that the degradation rate in the presence of titanium dioxide depends on the initial 2-amino-5-chloropyridine concentration in a

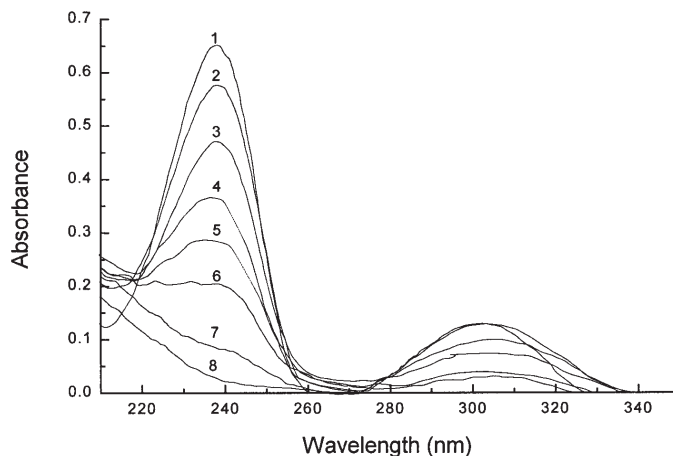


Fig. 2. UV Spectrum profiles during photocatalytic degradation of the 2-amino-5-chloropyridine (2.5 mmol/dm^3) in the presence of TiO_2 (2 mg/cm^3). Illumination time (h): (1) 0; (2) 0.5; (3) 1.0; (4) 2.0; (5) 3.5; (6) 5.5; (7) 8.0; (8) 9.0.

way that the rate constant k decreases with increasing initial concentration. This finding indicates that the degradation kinetics of 2-amino-5-chloropyridine are not of simple first-order but pseudo-first-order. Furthermore, the slopes of the lines and the k values presented in Table I show that the reaction rate constant decreases rapidly at lower initial substrate concentrations, while at higher initial concentrations, it decreases more slowly.

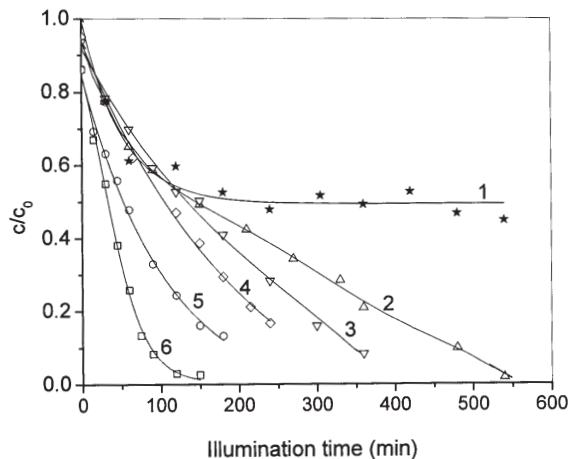


Fig. 3. Kinetic curves for the degradation of the pyridine moiety monitored by spectrophotometry (mmol/dm^3): (1) 2.5; (2) 2.5; (3) 2.1; (4) 1.5; (5) 1.0; (6) 0.5. Curve (1) direct photolysis; curves (2) – (6) in the presence of TiO_2 (2 mg/cm^3).

A high rate of the degradation of the initial compound does not necessarily indicate its complete mineralization. Namely, the formation of much more stable, and what is worse probably more toxic intermediates, is very common. For this reason a spectrophotometric method was used for monitoring the rate of the degradation of the pyridine moiety. It was

found that the UV spectrum of the investigated compound has two distinct absorption maxima in the range from 200 to 340 nm (Fig. 2). During illumination, Fig. 2, both the absorption maxima decrease which indicates the destruction of the pyridine moiety. The change in the concentration of the pyridine moieties during illumination are presented in Fig. 3, curves 2–6. From the obtained kinetic curves, it can be concluded that the time necessary for the elimination of chlorine (direct photolysis) is significantly lower (about 25 times) than the time necessary for the complete destruction of the pyridine moieties. This indicates that the chlorine elimination reaction dominates in the first part of the process, after which the reaction of the destruction of the pyridine moieties takes place *i.e.*, the degradation of all the pyridine intermediates.

TABLE I. Effect of the initial concentration (c_0) of 2-amino-5-chloropyridine on the photodegradation rate

c_0 /(mmol/dm ³)	$10^2 k/\text{min}^{-1}\text{§}$	r^\dagger	$t_{1/2}/\text{min}^\ddagger$
1.0	15	0.999	3.76
2.0	7.1	0.999	9.33
2.5	6.3	0.999	10.72
2.9	5.5	0.999	12.56

§First-order rate constant; † linear regression coefficient; ‡ half-life

The degradation of the pyridine moieties was also investigated by direct photolysis (Fig. 3, curve 1). As can be seen, complete degradation of the pyridine moieties does not occur, indicating the advantage of the application of heterogeneous photocatalysis.

TABLE II. Effect of the initial concentration (c_0) of 2-amino-5-chloropyridine on the direct photolysis rate

c_0 /(mmol/dm ³)	$10^4 k/(\text{mol dm}^{-3} \text{min}^{-1})\text{§}$	r^\dagger	$t_{1/2}/\text{min}^\ddagger$
1.0	1.33	0.998	3.41
1.5	1.32	0.999	5.39
2.0	1.28	0.999	7.39
2.5	1.11	0.999	10.96

§Zero-order rate constant; † linear regression coefficient; ‡ half-life

Monitoring the kinetics of photocatalytic degradation by means of the change in the pH has mainly been employed for the investigation of simple molecules, such as chloroform, tetrachloromethane or dichloromethane, where practically no intermediates are formed, and therefore the formation of hydronium ions directly corresponds to the kinetics of the degradation of the initial compound.³ This is not usually the case with more complex molecules where the change in the pH cannot be used for kinetic analysis, but, nevertheless, its monitoring during a photocatalytic process gives valuable insight into the net changes in the investigated system. Thus, the change in the pH monitored during the irradiation of a ≈ 2.5 mmol/dm³ 2-amino-5-chloropyridine solution (Fig. 4, curve 3) confirms that the process of chloride generation dominates since a sudden drop of pH occurs, although its value is higher than it should be if only hydrochloric acid were formed, indicat-

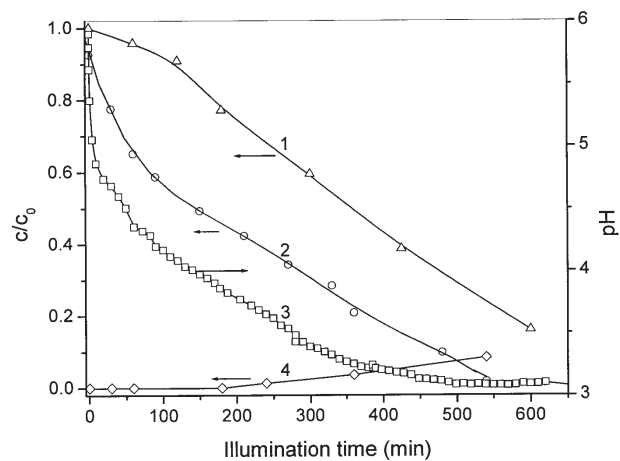


Fig. 4. Typical diagram of the degradation of 2-amino-5-chloropyridine in the presence of TiO_2 (2 mg/cm^3): (1) TOC; (2) normalized concentration of the pyridine moiety; (3) pH; (4) normalized nitrate concentration.

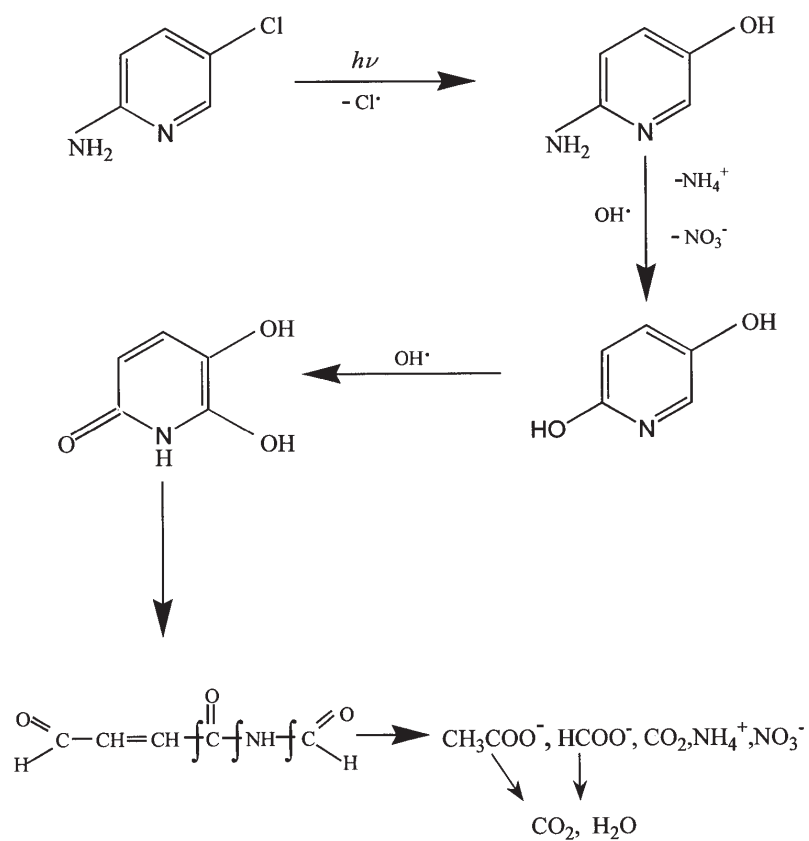


Fig. 5. Possible mechanism for the photocatalytic degradation of 2-amino-5-chloropyridine.

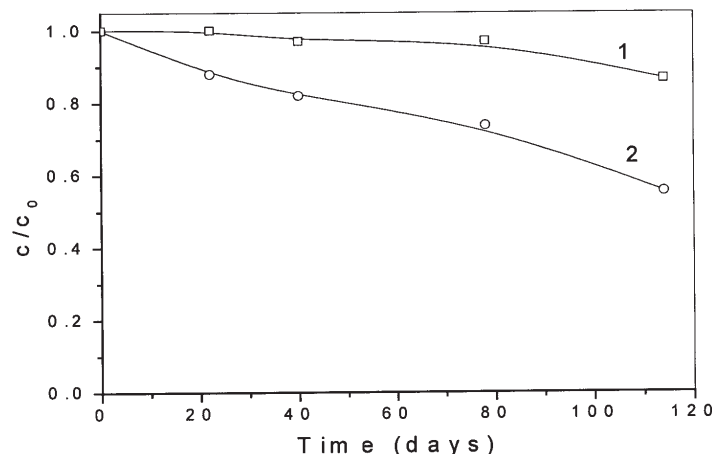


Fig. 6. Kinetics of the degradation of 2-amino-5-chloropyridine (2.5 mmol/dm³) in the absence of TiO₂ monitored by spectrophotometry: (1) in the dark; (2) in sunlight.

ing protonation of the pyridine nitrogen, as well as the formation of ammonium ions. The further decrease of pH is most likely due to the formation of formic, acetic and nitric acids. The evolution of nitrate was confirmed by ion chromatography (Fig. 4, curve 4), but only after three hours of illumination and in relatively low concentrations. The continuous decrease of pH value even after the complete degradation of the compound (20 h) indicates the gradual transformation of ammonium ions to nitrate.²

As it can be seen from the results of the TOC measurements (Fig. 4, curve 1), during the first part of the process, the change in TOC is small. The subsequent steady decrease of the TOC with time confirms the complete mineralization of the initial compound, as well as the intermediates formed during the process. After 9 h of irradiation (when all the pyridine moieties had been degraded, Fig. 4, curve 2), the initial TOC had been reduced by about 80 %, indicating possible presence of formic and acetic acids.

Taking into account the nature of some of the observed species and the rate of their disappearance, as well as literature data,^{2,3,12,15-17} the probable mechanism of the photocatalytic degradation of 2-amino-5-chloropyridine is shown in Fig. 5. As can be seen, in the first stage substitution of the Cl atom by an OH group takes place.^{3,12,16} After that the NH₂ group and one of the ring H atoms are substituted by OH radicals.¹⁷ The substituted amino group is further transformed to nitrogen containing inorganic ions (predominantly in the form of NH₄⁺).¹⁷ The parent compound, after transformation into a polyhydroxylic pyridine readily undergoes ring opening and further degradation to acetic and formic acid, carbon dioxide and nitrogen containing inorganic ions (predominantly in the form of NH₄⁺).^{2,15} By a further action of OH radicals, the acetic and formic acid are decomposed into CO₂ and H₂O.

In order to confirm the efficiency of the photocatalytic degradation, the degradation kinetics were monitored in the absence of TiO₂ in both the presence and absence of sunlight. It was found that the substrate decomposes spontaneously under sunlight but at a lower rate (Fig. 6, curve 2). After 115 days of exposition of substrate solutions to daily sunlight about 40 % of the

substrate had been degraded. The solutions protected from sunlight showed no change even after 80 days (Fig. 6, curve 1). These results indicate that, as was expected, the most efficient method for the destruction of the substrate is irradiation in the presence of TiO₂.

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ИЗВОД

ДИРЕКТНА ФОТОЛИЗА И ФОТОКАТАЛИТИЧКА РАЗГРАДЊА
2-АМИНО-5-ХЛОРПИРИДИНА

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Испитиване су директна фотолиза и фотокаталитичка разградња 2-амино-5-хлорпиридина, као модел једињења за пестициде који у свом молекулу имају пиридински прстен. Примењене су различите аналитичке технике – потенциометрија, за праћење рН и за настајање хлорида, спектрофотометрија за праћење разградње пиридинског прстена, јонохроматографија за праћење настајања нитрата и анализа укупног органског угљеника ради испитивања ефикасности процеса. Фотокаталитичка разградња је проучавана у воденим суспензијама титан(IV)-оксида уз озрачивање ултраљубичастом светлошћу. Нађено је да је реакција настајања хлорида нултог реда и да се одвија директном фотолизом, те се на тај начин разликује од процеса разградње пиридинског прстена, до ког долази у присуству титан(IV)-оксида. Промена рН у току разградње указује на настајање киселих интермедијера и нитрата поред хлорида. Такође је испитан и утицај почетне концентрације супстрата праћењем како реакције настајања хлорида, тако и реакције разградње пиридинског прстена. Нађено је да је разградња полазног једињења (2,5 mmol/dm³) директном фотолизом потпуна за око 20 минута, а пиридинског прстена применом фотокаталитичке разградње за око девет сати. На основу добијених података предложен је могућ механизам реакције.

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