

# Photodegradation of pyridylketoximes in methanolic solutions under UV–Vis radiation

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**Abstract** Photodegradation of the oximes of alkyl-2-, -3-, and -4-pyridylketones and identification of possible degradation products using LC–MS/MS and GC–MS techniques were performed. The influence of copper(II) and iron(III) ions on the stability of the oxime under UV–Vis radiation exposure were also studied. It was found that the photodegradation of the pyridylketoximes resulted in the photoisomerization, photofragmentation and photosubstitution to a pyridine ring. Based on these results, a hypothetical mechanism of photodegradation of pyridylketoximes was proposed.

**Keywords** Photodegradation · UV–Vis light · Pyridylketoxime · Cu(II) · Fe(III)

## Introduction

Oxime ligands containing a pyridyl ring are the most interesting group of compounds in the chemistry of metal complexes. These compounds are widely used as analytical reagents [1–3], in medicinal preparations [4, 5], as components of photodynamic herbicides [6] and in chemical trace metal analysis [7–9]. Moreover, pyridylketoximes play an important role in organic synthesis, e.g. of metallacrown complexes [10, 11], and as catalysts of the cleavage of carboxylic acid esters [12, 13]. Hydrophobic pyridyl ketoximes have also been proposed as a new type of

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ligand for the selective removal of metal using liquid–liquid extraction methods [14–16].

Long-term application of chemical compounds, especially metal extractants, has resulted in the development of a wide variety of approaches to the study of their thermal, chemical and photochemical stability. Resistance to radiation is a very important parameter which determines the application of the organic compound as the complexing agent, especially in spectroscopic analysis and an extraction process.

Photochemical reactions of oximes have received considerable attention. Available literature on the photochemistry of oxime suggests that syn-anti isomerization is the major process and is affected by the condition (type of solvent and the presence of added species such as salts) and the concentration of the oxime. Additionally, aldo- and ketoximes undergo other photoreactions: dimerism and Beckmann rearrangement, though the photodegradation studies of pyridyl oximes is limited to photoisomerization of oximes of pyridine-4-carboaldehyde [17].

The aim of this work was to study the photodegradation of 2-, 3- and 4-pyridine ketoximes in methanol. The influence of the length of alkyl chain, the position of the oxime substituent, and the presence of complexed metal ( $\text{Cu}^{+2}$  and  $\text{Fe}^{+3}$ ) on the photostability of the pyridineketoximes were also analyzed. Determination of the kinetics of the process and the identification of possible photo-products were carried out using UV–Vis spectroscopy and LC–MS/MS or GC–MS methods.

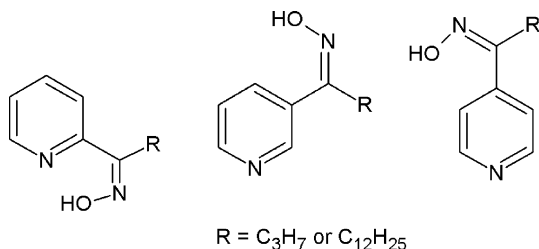
## Materials and methods

### Reagents

The oximes of 1-(2-pyridyl)butan-1-one (2pc3), 1-(2-pyridyl)tridecan-1-one (2pc12), 1-(3-pyridyl)butan-1-one (3pc3), 1-(3-pyridyl)tridecan-1-one (3pc12), 1-(4-pyridyl)butan-1-one (4pc3) 1-(4-pyridyl)tridecan-1-one (4pc12) (Scheme 1.) were synthesized with yields: 2pc3—42 %, 2pc12—38 %, 3pc3—53 %, 3pc12—73 %, 4pc3—71 %, 4pc12—80 % (purity 99.8 %; HPLC-ESI,  $^1\text{H}$  NMR) [12, 14]. The structure of obtained oximes were confirmed the  $^1\text{H}$  and  $\text{C}^{13}$  NMR technique. Electronic absorption spectra of the oximes are given in Table 1.

Methanol (p. a., Chempur) was used as diluent. *N,O*-bis(trimethylsilyl)acetamide (96 %, Sigma Aldrich) and pyridine (p.a., Sigma Aldrich) were used as derivatization reagents. Chloride salts of metals and other chemicals were of analytical grade. MS-grade methanol (Sigma Aldrich) with addition of ammonium acetate

**Scheme 1** Structural formula of studied pyridylketoximes



**Table 1** Electronic absorption spectral data of the pyridylketoximes in methanol solution

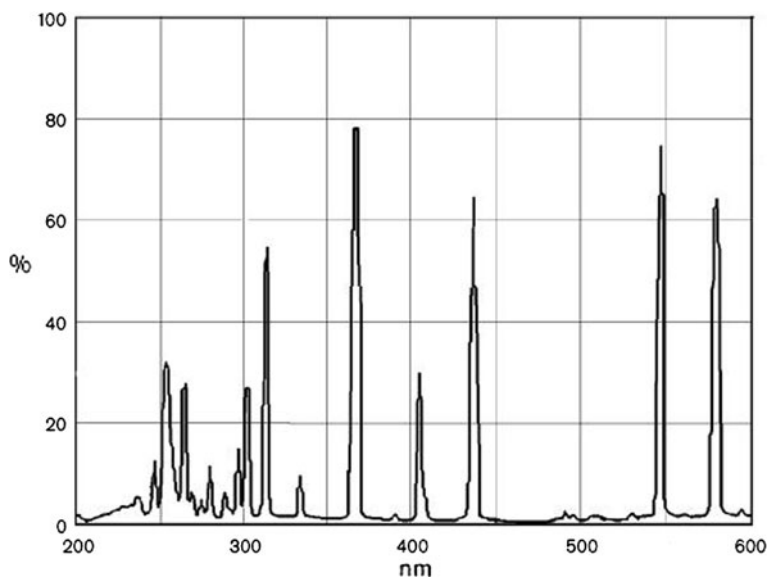
Oxime	$\lambda_{\max}$ (nm)	Log $\epsilon$ (dm <sup>3</sup> /mol cm)
1-(2-Pyridyl)butan-1-one oxime	205	4.07
	235	3.80
	278	3.87
1-(2-Pyridyl)tridecan-1-one oxime	206	4.02
	238	3.98
	271	3.90
1-(3-Pyridyl)butan-1-one oxime	205	4.19
	244	4.17
1-(3-Pyridyl)tridecan-1-one oxime	203	4.04
	237	3.90
1-(4-Pyridyl)butan-1-one oxime	204	4.08
	254	4.03
1-(4-Pyridyl)tridecan-1-one oxime	203	3.99
	254	3.83

(Sigma Aldrich) were used as a mobile phase for LC–MS. The LC-grade water [below 1 ( $\mu\text{S}/\text{cm}$ )] was prepared by reverse osmosis in a Demiwa 5ROI system from Watek (Ledec and Sazavou, Czech Republic), followed by double distillation from a quartz apparatus. Only freshly distilled water was used.

#### Photodegradation procedure

Oxime or oxime:metal samples ( $1 \times 10^{-3}$  mol/dm<sup>3</sup>) in methanol were irradiated in a Heraeus photoreactor of 120 cm<sup>3</sup> volume containing a medium pressure mercury lamp TQ 150 W (Heraeus) and quartz filter. The lamp was positioned within the inner part of the photoreactor, and cooling water was circulated through a Pyrex jacket surrounding the tube. Argon was passed through the solutions with a stationary flow of 2 cm<sup>3</sup>/min at 22–23 °C during radiation. Agitation of the reaction mixture was provided by a magnetic stirrer. The photodegradation was repeated two times. The photon fluence of the mercury lamp was determined by chemical actinometry using the potassium ferrioxalate and the lamp irradiated the reaction solution with the intensity of 0.071  $\mu\text{einstein}/\text{dm}^3\text{min}$ . Emission of the polychromatic lamp is shown in Fig. 1.

After photodegradation, the samples were analyzed using LC–MS/MS and UV–Vis techniques in 0, 5, 10, 15, 20, 25, 30, 45, and 60 min of radiation. Additionally, the samples obtained after 60 min of the photodegradation were analyzed using the GC–MS technique. Quantitation and identity confirmation of the degraded oximes were attained by electrospray positive ionization LC–MS/MS in multiple reactions monitoring the MRM mode. The degradation products were characterized by mass spectrometry (LC–MS/MS and GC–MS).



**Fig. 1** Emission spectrum of the medium pressure mercury lamp TQ 150 W

### GC-MS analysis

GC-MS analyses were performed using a Varian CP3800 gas chromatography with a 4000 MS mass spectrometer. Helium ( $1 \text{ cm}^3/\text{min}$ ) was used as the carrier gas. The transfer line and trap temperatures were 170 and 150 °C, respectively. A VF-5 ms Varian CP8944 ( $30 \text{ m} \times 0.25 \text{ mm} \times 0.39 \text{ mm}$ ) column was used. After a sample injection at 50 °C (injection port 250 °C), the oven temperature was increased to 330 °C at 10 °C/min.

To enable the detection of the oxime, each sample ( $1 \text{ cm}^3$ ) was derivatised by addition of  $0.3 \text{ cm}^3$  of pyridine and  $0.3 \text{ cm}^3$  of *N,O*-bis(trimethylsilyl)acetamide (BSA) and heated (80 °C) for 30 min. Changes in the value of the components were performed based on changes in the peaks area.

### LC-MS/MS analysis

LC analysis was performed using the UltiMate 3000 RSLC chromatographic system from Dionex (Sunnyvale, CA, USA). Samples of  $5 \mu\text{L}$  were injected into a  $100 \times 2.1 \text{ mm}^2$  I.D. analytical column packed with  $1.9 \mu\text{m}$  Hypersil Gold C18 RP from Thermo Scientific (USA). The mobile phase used for the analysis consisted of 5 mmol/L ammonium acetate in water (A) and methanol (B) at a flow rate of 0.25 mL/min. The following gradient was used: 0 min 80 % B, 1.5 min 100 % B, 4 min 100 % B.

The LC system was connected to the API 4000 QTRAP triple quadruple mass spectrometer from AB Sciex (Foster City, CA, USA). The Turbo Ion Spray source

operated in the positive ion mode. Oximes and degradation products were detected using the following settings for the ion source and mass spectrometer: curtain gas 10 psi, nebulizer gas 40 psi, auxiliary gas 40 psi, temperature 400 °C, ion spray voltage 5,500 V, and declustering potential 40 V. The complexes were infused into the ESI source using a Harvard pump at a flow rate of 10  $\mu$ L/min.

### Spectrophotometric analysis

The absorption spectrum of solutions before and after degradation was carried out in the UV–Vis region (200–999 nm.) by using a UV 1601PC Shimadzu spectrophotometer.

## Results and discussion

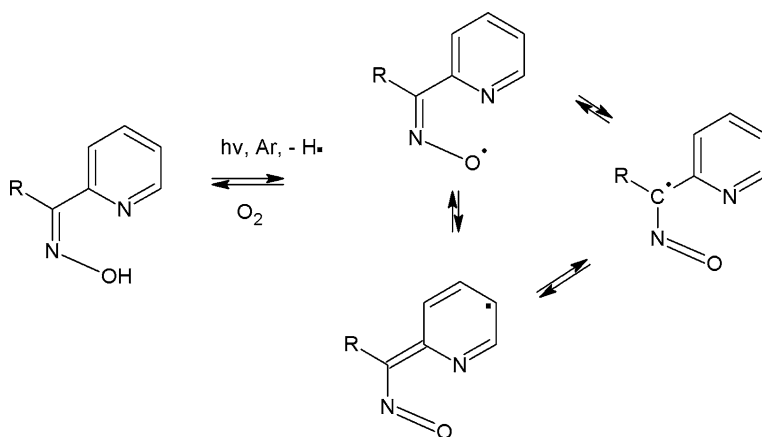
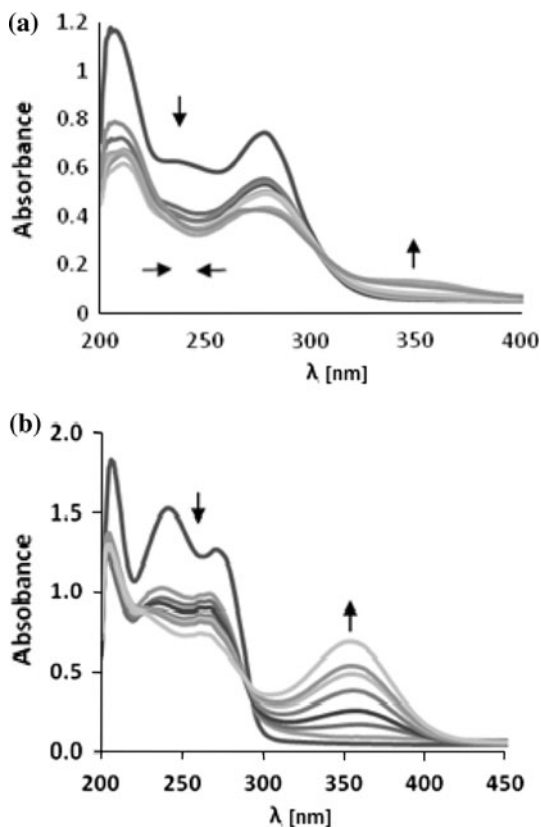
### Oximes photodegradation

As a result of exposures to UV–Vis radiation, many changes were seen both on the LC–MS/MS chromatograms and UV–Vis spectrums. UV–Vis analysis of the oxime of 1-(2-pyridyl)butan-1-one during radiation in methanol shows the dramatic decrease of the signal intensity just after the first 5 min (0.355  $\mu$ einstein/dm<sup>3</sup>min) of radiation, and further photoreaction causes the appearance of band at 350 nm (Fig. 2a). The results suggest a very fast photoreaction and, probably, the creation of photoproducts. The oxime of 1-(2-pyridyl)tridecan-1-one also degrades under exposure to UV–Vis radiation; however, the process is not similar to that for the oxime of 1-(2-pyridyl)butan-1-one. Spectroscopic analysis also noted the dramatic decrease in the intensity of the ligand signals resulting in the formation of excited species of the oxime, though after 10 min of radiation (0.71  $\mu$ einstein/dm<sup>3</sup>min), a new structure absorption band appears with a maximum at 350 nm, which increases with the time of UV–Vis exposition (Fig. 2b).

The new excited structure of the 2-pyridylketoxime is probably iminoxy radical (Scheme 2.), which is typical for oxime and nitro-compounds [18–22]. Literature confirms that the increase of alkyl size can be attributed to a progressive relief of steric strain on the loss of a hydrogen atom to form an iminoxy radical. Increase of the stability of the iminoxy radical with the alkyl chain size confirms worse efficiently photoreaction in the case of 1-(2-pyridyl)butan-1-one oxime (low intensity signal at 350 nm.) than in the case of 1-(2-pyridyl)tridecan-1-one oxime.

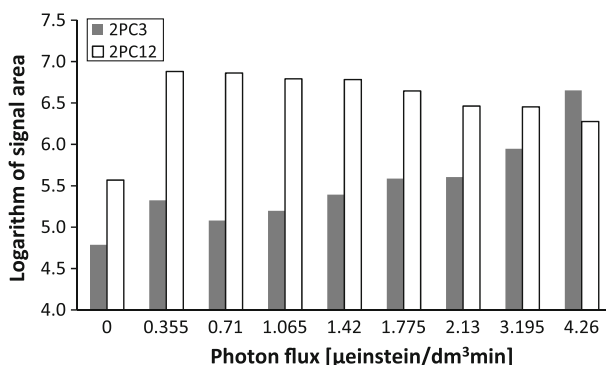
The LC–MS/MS analysis of the solution containing the studied oxime before and after the UV–Vis exposures showed the increase of the signal intensity. LC/MS/MS is a very powerful technique capable of analyzing both small and large molecules of various polarities, but the ESI ionization method is very sensitive to the pH change of the solution (e.g., the increase of pH positively influences the cation signal intensity). In our study, the increase of the signal area could be combined with the hydrogen radical addition to oxime molecules or with the change of geometric structure of the studied oximes. The oxime of 1-(2-pyridyl)tridecan-1-one achieved the maximum of excited species after 5 min of radiation (0.355  $\mu$ einstein/dm<sup>3</sup>min),

**Fig. 2** Spectroscopic (UV–Vis) study of the solutions during UV–Vis radiation of oxime of 1-(2-pyridyl)butan-1-one (a) and oxime of 1-(2-pyridyl)tridecan-1-one (b)



**Scheme 2** Iminoxy radical formation

and after that time, the further radiation causes gradual degradation, whilst the oxime of 1-(2-pyridyl)butan-1-one did not reach the maximum even after 60 min of photoreaction (Fig. 3.). The slower increase in signal intensity in the case of oxime



**Fig. 3** Changes of area of the signal of oxime of 1-(2-pyridyl)butan-1-one ( $m/z = 165.4$  ( $[M+H]^+$ ) and oxime of 1-(2-pyridyl)tridecan-1-one ( $m/z = 291.5$  ( $[M + H]^+$ ) during UV-Vis radiation

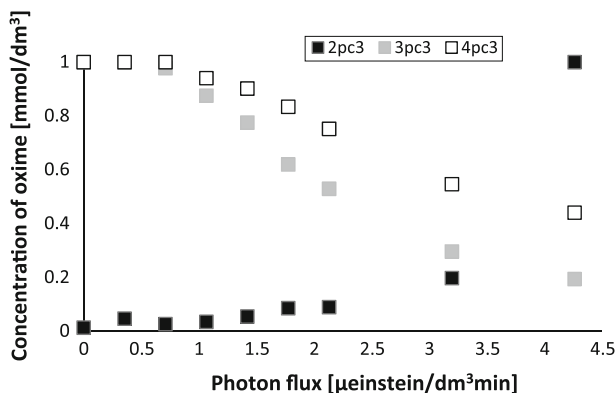
of 1-(2-pyridyl)butan-1-one in comparison to 1-(2-pyridyl)tridecan-1-one oxime may also be combined with the difference in the initial isomer structure (*E-Z*) of both oximes. *Z*-isomer is stabilized by an intramolecular hydrogen bridge which reduces the process of the ionization of pyridine nitrogen and/or photodegradation of the oxime.

Addition of the hydrogen radical during radiation was also observed and confirmed by the presence of the pseudomolecular ion with  $m/z = 165$  or  $292([M + H]^+)$ .

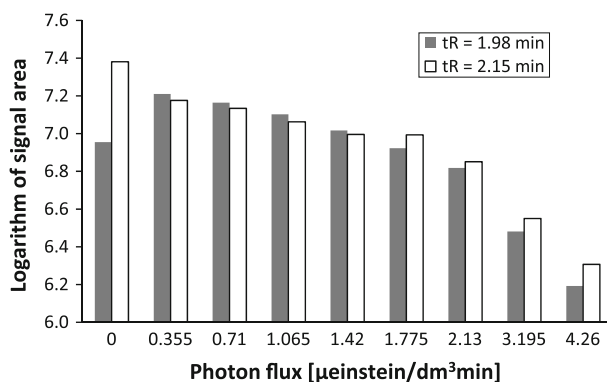
Change in the distance between pyridine nitrogen and oxime substituent influences the mechanism of photodegradation. UV-Vis analyses of the oxime of 1-(3-pyridyl)butan-1-one and oxime of 1-(4-pyridyl)butan-1-one, similar to the oxime of alkyl-2-pyridylketone, shows the dramatic decrease of the signal intensity just after the first 5 min of radiation ( $0.355 \mu\text{einstein}/\text{dm}^3\text{min}$ ). However, no new signal was observed. Despite the fact that the iminoxy radicals formation of 3- and 4-pyridyl oximes has been confirmed by other researchers, the presence of the band at  $\lambda_{\text{max}} = 350 \text{ nm}$  on the oxime spectrum is not visible. Probably, the presence of the band in the case of 2-pyridyl oximes is a result of not only the resonance stabilization of iminoxy radical but also by blocking of the unpaired electron of the pyridine nitrogen atom (blocking by hydrogen radical derived from oxime moiety or from the ionized methanol molecule). Similarly, the UV-Vis spectrum was observed during studies of copper-(2-pyridyl oxime) complexes in which the metal coordination was through both oxime oxide and pyridine and imine nitrogens.

LC-MS/MS analysis of the solution containing the oxime of 1-(3-pyridyl)butan-1-one or the oxime of 1-(4-pyridyl)butan-1-one before and after UV-Vis exposures did not show an increase of the signal area, and, during the first 15 min ( $1.065 \mu\text{einstein}/\text{dm}^3\text{min}$ ) of UV-Vis radiation exposure, both oximes exhibited high resistance to radiation. Continuation of the radiation resulted in gradual photodegradation to 43 and 57 % of the oximes 3pc3 and 4pc3, respectively (Fig. 4).

Different reactions were observed during photodegradation of hydrophobic 3- and 4-pyridylketoximes. LC-MS/MS analysis of the oximes before



**Fig. 4** Rate of photodegradation of the oximes of 1-(2-pyridyl)butan-1-one (2pc3), 1-(3-pyridyl)butan-1-one (3pc3) and 1-(4-pyridyl)butan-1-one (4pc3) under exposure to UV–Vis radiation in methanol

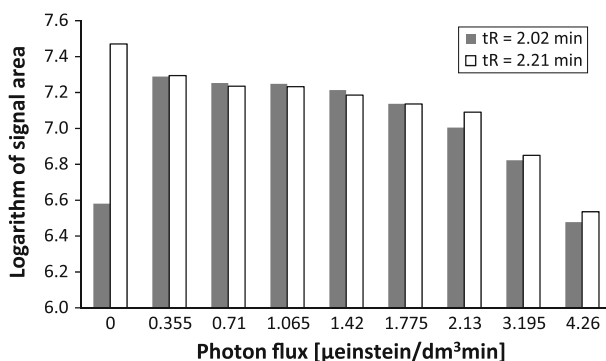


**Fig. 5** Changes of area of the signal isomers of 1-(3-pyridyl)tridecan-1-one oxime during UV–Vis radiation (LC–MS/MS)

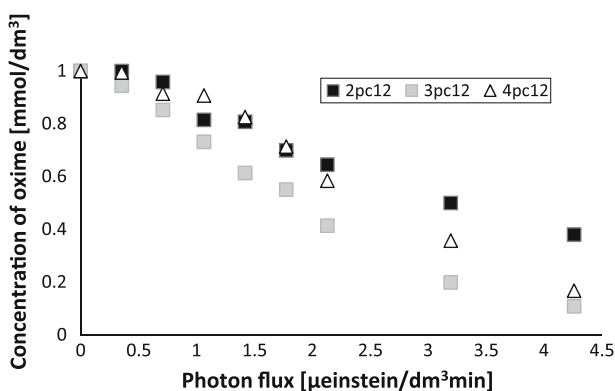
photodegradation showed the presence of two isomers in the solutions. It is very difficult to determine the type of isomer (geometric involves a C=N bond or resulting from the steric effects of the alkyl chain) because the fragmentation of the pseudomolecular ion  $[M+H]^+$  (ESI; LC–MS/MS) and molecular ion  $M^+$  (EI, GC–MS) of each isomer is similar. Differences are only found in the intensity of the fragmentation ions,  $m/z = 52$  and  $67$ .

Chromatographic analysis of the solution obtained after exposure to UV–Vis radiation, both for the oxime of 1-(3-pyridyl)tridecan-1-one and for the oxime of 1-(4-pyridyl)tridecan-1-one, showed changes in the signal area of each isomer (Figs. 5, 6). Initially, the isomer at retention times 2.21 (4pc12) and 2.15 (3pc12) predominates. After 5 min of radiation ( $0.355 \mu\text{einstein}/\text{dm}^3\text{min}$ ), both isomers reached the equilibrium, and further radiation caused a similar rate of photodegradation.





**Fig. 6** Changes of area of the signal isomers of 1-(4-pyridyl)tridecan-1-one oxime during UV–Vis radiation (LC–MS/MS)

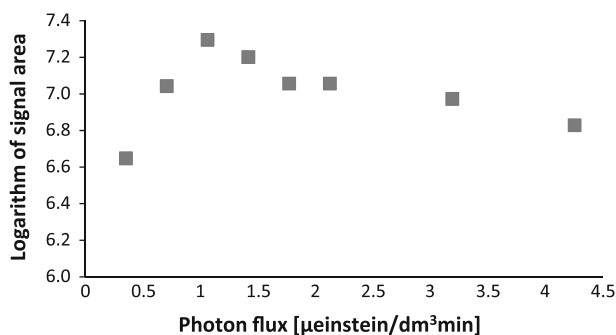


**Fig. 7** Rate of photodegradation of the oximes of 1-(2-pyridyl)tridecan-1-one (2pc12), 1-(3-pyridyl)tridecan-1-one (3pc12) and 1-(4-pyridyl)tridecan-1-one (4pc12) under exposure to UV–Vis radiation in methanol

Comparing the pyridylketoximes containing the dodecyl alkyl chain, it can be concluded that the rate of the photodegradation depends mainly on the position of the oxime group in the pyridine ring (Fig. 7). The compounds with the oxime group at position 2 has the highest resistance to radiation, whilst 3-pyridylketoxime is the most sensitive to UV–Vis radiation. Similar dependence is observed for the oximes with a propyl alkyl chain, but in the case of alkyl-2-pyridyl oxime, the reduction of the chain length has a positive effect on the photoresistance of the compound or only causes photoisomerization.

#### By-products analysis

Radiation of the 1-(2-pyridyl)butan-1-one oxime and 1-(2-pyridyl)tridecan-1-one oxime led mainly to photoisomerization products. However, in the case of the oxime of 1-(2-pyridyl)butan-1-one, the photosubstitution product was also observed



**Fig. 8** Rate of formation of the photosubstitution product after radiation of the 1-(2-pyridyl)butan-1-one oxime based on changes of peaks areas (LC–MS/MS analysis,  $t_R = 0.99$ ; photosubstitution by methyl group)

(Fig. 8). Based on the fragmentation spectrum and the mass of pseudo-molecular ion, it can be inferred that the photosubstitution is in the pyridine ring by the methyl group.

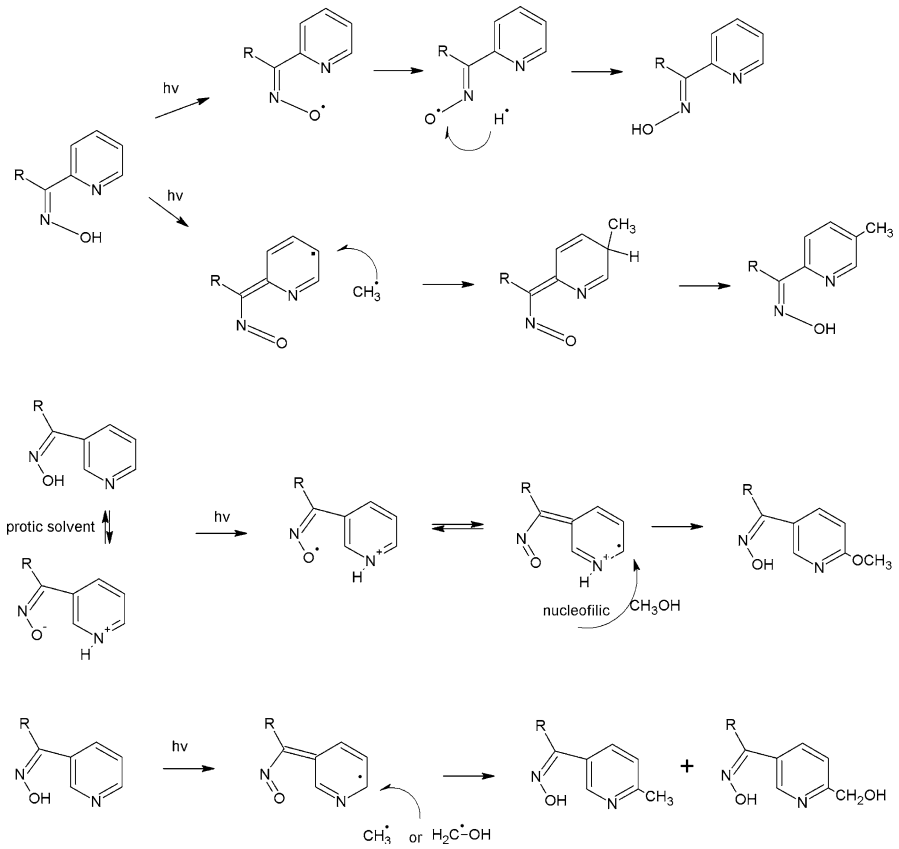
Photosubstitution may be caused by a radical reaction between excited oxime and methanol molecules (Scheme 3). Photodegradation of oxime of 1-(2-pyridyl)tridecan-1-one is combined only with fragmentation of alkyl chain, but the mass of the removed fragment is not higher than 29 g/mol of oxime. Fragmentation causes the destruction of the initial compounds; however, the formation of oxime with the decyl or even octyl alkyl chain does not change the application of the oxime as a metal ligand.

Despite the fact that oximes of alkyl-3- or 4-pyridylketones, especially with a long alkyl chain, are less resistance to radiation, photodegradation is not combined with photofragmentation of the oxime substituent, but with a photosubstitution to the pyridine ring.

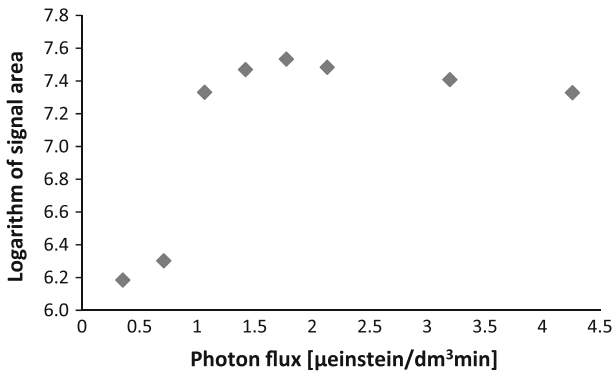
In the case of oximes of 1-(3-pyridyl)butan-1-one, 1-(4-pyridyl)butan-1-one, 1-(3-pyridyl)tridecan-1-one and 1-(4-pyridyl)tridecan-1-one, the photosubstitution is by alkoxy radicals (Figs. 9, 10). Additionally, 3-pyridylketoximes are also photosubstituted by the methyl or hydroxymethyl groups.

Identification of the by-products was done based on the fragmentation of pseudomolecular ions  $[M+H^+]$ . For example, the photosubstitution by hydroxymethyl group is combined with H ( $m/z = 1$ ) and CHO ( $m/z = 29$ ) release, while the MS fragmentation of methoxy group is caused by  $\cdot\text{OCH}_3$  ( $m/z = 30$ ) removal. The results of the by-product determination based on the LC–MS/MS analysis are presented in Table 2.

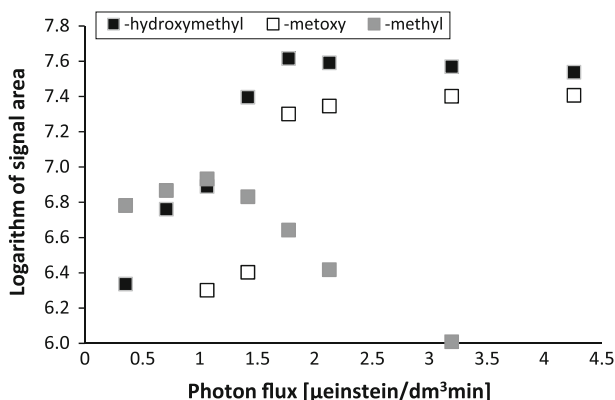
The mechanism of photosubstitution to the pyridine ring in the presence of oxime moiety seems to be different from that for other pyridine derivatives. The UV radiation of pyridine-3- and -4-pyridinecarboxylic acids, esters and amides, depends on the pH of alcoholic solution and also leads to hydroxyalkylation and alkoxylation [23–29]. However, the hydroxymethylation is combined with the photoreduction (radical not ionic reaction) to the alkyl substituent. Sugiyama et al. [28], Minisci [30] and Citterio et al. [31] pointed out that photoalkylation to the pyridine ring or to



**Scheme 3** Mechanism of photodegradation of pyridylketoximes



**Fig. 9** Rate of formation of the photosubstitution product after radiation of the 1-(4-pyridyl)tridecan-1-one oxime based on changes of peaks areas (LC-MS/MS analysis,  $t_R = 2.26$ ; photosubstitution by methoxy group)



**Fig. 10** Rate of formation of the photosubstitution products (methyl ( $t_R = 1.26$ ) (filled square), methoxy ( $t_R = 2.46$ ) (open square) and hydroxymethyl ( $t_R = 1.94$ ) (filled square) after radiation of the 1-(3-pyridyl)tridecan-1-one oxime based on changes of peaks areas (LC–MS/MS analysis)

**Table 2** Results of photosubstitution products determination based on the LC–MS/MS analysis (by-products observed only at 20 min of radiation)

Oxime	Photosubstituent	$[M+H^+]$	Fragmentation signals (m/z)
1-(3-Pyridyl)butan-1-one oxime	$-\text{OCH}_3$	195.8	(181.3; 119.7; 106.9)
1-(4-Pyridyl)butan-1-one oxime	$-\text{OCH}_3^a$	195.4	(181.3; 119.6; 107)
	$-\text{CH}_3^a$	179.5	(162.3; 121.4; 87.6)
1-(3-Pyridyl)tridecan-1-one oxime	$-\text{OCH}_3$	321.6	(306.6; 276.1; 249.6; 163.2; 107.3; 87.2)
	$-\text{CH}_3$	305.5	(253.8; 148.7; 133.1; 121.2)
	$-\text{CH}_2\text{OH}$	321.8	(306.4; 221.4; 163.4; 149.5; 77.3; 60.2)
1-(4-Pyridyl)tridecan-1-one oxime	$-\text{OCH}_3$	321.5	(306.6; 304.5; 149.3; 107.2; 87.4)

other aromatic N-heterocycles occurs through hydrogen abstraction by the excited protonated pyridine derivatives, while the addition of mineral acids caused the alkylation to 4-position (exciting pyridinium form) and the alkoxylation to 6-position resulting in excimer formation. In the case the oxime of alkyl -3- and -4-pyridyl ketone methoxy photosubstitution, the hydrogen migration is probably favored by the protic solvent [32]. A similar mechanism causes methyl substitution through the reduction of the hydroxyalkyl fragment. Methyl and hydroxyalkyl substitution of 3-pyridylketoximes and methyl substitution of 2-pyridylketoximes can also result in the radical recombination of hydroxymethyl (without water molecule removal) or methyl radical with iminoxy radical. Photoreactions of pyridylketoximes could proceed in the following scheme: the 2-pyridylketoxime photosubstitution by the methyl group through the addition of the methanol molecule to the excited pyridine ring and then water molecule removal is possible but only by moving of the hydrogen ion from oxime to pyridine nitrogen.

## Photodegradation of oxime in the presence of metal

Photodegradation of pyridylketoximes in the presence of copper(II) and iron(II) chloride was performed for the oximes of 1-(2-pyridyl)butan-1-one, 1-(3-pyridyl)butan-1-one and 1-(4-pyridyl)butan-1-one. Coordination of copper(II) ions by 2-pyridylketoximes was mainly through the chelate mechanism forming stable copper(II) complexes [14]. The location of oxime substituent at position 3 and 4 in the pyridine ring enabled coordination through a solvating mechanism with stabilization by an intermolecular hydrogen bond. The complexation of iron ions is only by nitrogen (pyridine and imine) coordination.

Electronic spectra of the methanolic solutions of mixture of oxime of 1-(4-pyridyl)butan-1-one and copper(II) chloride in molar ratio 1:1 before photodegradation show an absorption above the 700-nm wavelength range which confirms the presence of the coordinated metal in the solution. After 1 min exposure to UV–Vis radiation ( $0.071 \mu\text{einstein}/\text{dm}^3\text{min}$ ), the band disappeared, though the band between 290 and 330 nm was observed, suggesting small amounts of the coordinated copper ions. After 10 min radiation ( $0.710 \mu\text{einstein}/\text{dm}^3\text{min}$ ), the whole complex is destroyed and only the spectrum of the free oxime is observed. Changes in the UV–Vis spectra show a complex destruction and then ligand photodegradation, but in the presence of copper(II) ions, the photodegradation is 25.5 % whilst metal absence causes 43 % photodegradation.

Coordination of iron(III) chloride also positively influences the photostability of the 1-(4-pyridyl)butan-1-one oxime (only 38 % photodegradation) and, after 5 min radiation ( $0.355 \mu\text{einstein}/\text{dm}^3\text{min}$ ), destruction of the complex was also observed (disappearance of the complexes band at  $\lambda_{\text{max}} = 358 \text{ nm}$ ).

Complexes photodestruction or structure decomposition causes the photoreduction of the copper(II) ( $\text{Cu}^{+2} \rightarrow \text{Cu}^+ \rightarrow \text{CuO}$ ) [33–35] and iron(III) ions ( $\text{Fe}^{+3} \rightarrow \text{Fe}^{+2}$ ) [36]. During tests, a precipitate of CuO molecules resulting in  $\text{Cu}^{+2}$  of photoreduction after destruction of the complex was not observed; however, there is possibly a reaction between CuO and the methanol molecule resulting in formaldehyde formation [34, 35]. Unfortunately, the volatility of the formaldehyde did not enable confirmation of the reaction. Photoreduction of iron(III) chloride causes the formation of soluble iron(II) compounds [36]. Photodegradation of the complexes of 1-(3-pyridyl)butan-1-one oxime with copper(II) and iron(III) chloride, similar to 4-pyridylketoxime, is combined with complexes destruction after 10 min of radiation ( $0.710 \mu\text{einstein}/\text{dm}^3\text{min}$ ), and an increase in the resistance to radiation is also observed. In the presence of copper(II) or iron(III) ions, the photodegradation of 1-(3-pyridyl)butan-1-one oxime is 28.8 or 43.1 %, respectively, whilst metal absence causes 57 % photodegradation.

Photodegradation of the copper(II) complex with 1-(2-pyridyl)butan-1-one oxime confirms high stabilization of the adducts. During UV–Vis radiation, decomposition of the complex structure was mainly observed. Similar results were observed on the MS (ESI) spectrum obtained before and after radiation (Table 3.). MS analysis also showed, for the copper(II) complex, the presence of a photosubstitution product and, for the iron(III) complex, an exchange of chloride ions to methanol molecules.

**Table 3** Results of spectroscopic and MS (ESI) analysis of solutions of copper(II) and iron(III) complexes with 1-(2-pyridyl)butan-1-one oxime before and after irradiation

Complexes	Time of irradiation (min)	MS (ESI) ions (m/z)	UV-Vis bands (nm)
CuCl <sub>2</sub> -oxime	0	228 [HLCu] <sup>+</sup>	304
		391 [(HL) <sub>2</sub> Cu] <sup>+</sup>	707
		691 [(HL) <sub>3</sub> Cu <sub>2</sub> Cl <sub>2</sub> ] <sup>+</sup>	
	60	227 [LCu] <sup>+</sup>	330
		424 [(HL) <sub>2</sub> CuH <sub>2</sub> (CH <sub>3</sub> O)] <sup>+</sup>	680
		489 = 424 + Cu	
FeCl <sub>3</sub> -oxime	0	369 [HL(CH <sub>3</sub> OH) <sub>3</sub> FeCl(H <sub>2</sub> O)] <sup>+</sup>	305
		440 [(HL) <sub>2</sub> Fe(III)Fe(II)] <sup>+</sup>	415–600
		549 [(HL) <sub>3</sub> Fe(III)] <sup>+</sup>	
		636 [(HL) <sub>3</sub> Fe(III)Fe(II)(CH <sub>3</sub> OH)] <sup>+</sup>	
	60	664 [(HL) <sub>3</sub> Fe(III)Fe(II)(CH <sub>3</sub> OH) <sub>2</sub> ] <sup>+</sup>	
		636 [(HL) <sub>3</sub> Fe(III)Fe(II)(CH <sub>3</sub> OH)] <sup>+</sup>	400
			526

## Conclusion

Photodegradation of the pyridylketoximes depended on the position of the oxime group in the pyridine ring. The compounds with the oxime group at position 2 were the most resistance to radiation, whilst 3-pyridylketoxime was the most sensitive. In the case of alkyl-2-pyridyl oxime, reduction of chain length only caused photoisomerization.

Identification of possible degradation products using chromatographic techniques were performed and the results showed that photodegradation of pyridylketoximes resulted in photoisomerization, photofragmentation and photosubstitution to the pyridine ring. Based on these results, a hypothetical mechanism of photodegradation of the pyridylketoximes was proposed. The influence of copper(II) and iron(III) ions on the stability of the oxime under UV-Vis radiation exposure was also studied and the results confirmed the strong effect of coordination in the case of 2-pyridylketoxime. In the case of the 3- and 4-pyridylketoximes, radiation of UV-Vis radiation led to destruction of the solvating complexes after 10 min (0.710 μeinstein/dm<sup>3</sup>min) of radiation. However, the presence of metal ions also caused less oxime photodegradation in comparison to radiation of free ligands.

Resistance to radiation is a very important parameter which determines the application of the organic compound as the complexing agent, especially in spectroscopic analysis and an extraction process. In the case of pyridylketoxime, the photosubstitution to the pyridine ring by alkyl or hydroxylalkyl moiety can decrease a basicity of pyridine nitrogen and simultaneously reduce stability constants of metal-pyridylketoxime complexes. On the other hand, the photomethoxylation can increase a basicity of pyridine nitrogen and increase an ability of oxime to

protonation that has a negative influence on copper(II) complexation by 3- and 4-pyridylketoximes. The presence of other groups, especially alkoxy-, changes the molar absorptivity and maximum absorption wavelength of oximes or complexes with metal, which are very important during complexometric or colorimetric analysis. The positive aspect of the photosubstitution and photoisomerization of pyridineketoximes is a possibility to synthesize pyridine derivatives when the reaction under “dark conditions” is impossible or very difficult.

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