

Photostability of hydrophobic amides of pyridinecarboxylic acid as copper extractants from chloride media

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Abstract

The photostability of *N*-alkyl and *N,N*-dialkylpyridine-3-carboxamide, and *N*-alkyl and *N,N*-dialkylpyridine-2-carboxamide, and their copper complexes were studied. The obtained results indicated the influence of light (UV and vis) on the stability of pyridinecarboxamides. The degree of photodegradation depended on the type of solvent, the presence of water, hydrochloric acid or air in the solution. Also, the structure of compounds (the number and position of the amides group, structure of the amides carbon chain) influenced amides photostability. Products of photofragmentation of amides groups and photosubstitution at the pyridine ring were identified. Influence of ions of copper(II) and chloride during the photodegradation of copper complexes with pyridinecarboxamide was analyzed.

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1. Introduction

Copper(II) chloride can form complexes with pyridine and its derivatives in water, ethanol and aprotic solvents [1,2]. Pyridine derivatives with electron-attracting substituents in the ring, which are weak basic organic compounds, are used to transfer copper(II) ions from the chloride media to organic solutions. Esters and amides of pyridinemono- and dicarboxylic acids have been proposed by ZENECA (early ICI) for copper extraction from concentrated chloride solutions [3]. Equilibrium studies of extraction for hydrophobic pyridinemonocarboxamides show that these compounds are stronger copper(II) extractants from chloride solutions at pH >3 than pyridinecarboxylic acid esters [4]. The extraction abilities of pyridinecarboxamides depend on the structure, position and number of amide groups in the pyridine ring. Amides with one alkyl group are stronger extractants than amides with two alkyl chains. However, these “strong” extractants and their complexes with copper(II) are slightly dissolved in hydrocarbon diluents. Pyridinecarboxamides with *N,N*-dialkylamide groups are well soluble in organic solvents.

It was found that during the copper(II) extraction from chloride solutions, in the presence of amide excess, *N*-alkylpyridine-3-carboxamides form CuCl_2L_2 complexes (L-ligand), though *N,N*-dialkylpyridine-3-carboxamides can form two complexes CuCl_2L_2 or CuCl_2L_3 [4,5].

The resistance of the extractants to light is important during industrial extraction processes when extraction and stripping are carried out in installations with open mixers and settlers in countries where exposure to light is unavoidable. Previous studies indicated that hydroxyoxime extractants degraded on exposure to light and the rate of photodegradation was influenced by temperature, the presence of water and sulphuric acid [6–8]. Earlier works have shown that hydrophobic esters of pyridinecarboxylic acids and their copper-complexes degraded under exposure to light [9]. The influence of solvent type was also observed. Diester degraded faster than mono-ester with the analogy group. Increase of photodegradation caused the presence of 2-ethylhexyl groups. Also, the presence of hydrochloride acid and water influenced the stability of esters. The photodegradation of extractants and their copper-complexes confirmed the impact of Cu^{2+} and Cl^- on the rate of photoreaction.

The photoreactivity of pyridinecarboxamides (picolinamide, nicotinamide and isonicotinamide) in alcohol and alcohol–acid

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solutions were studied [10,11]. In alcoholic solution, these compounds undergo photosubstitution (alkoxylation, hydroxyalkylation and alkylation at pyridine ring) and photodegradation. The methylation of pyridine-3-carboxamide in the presence of mineral acid occurs effectively at lower concentrations of acid but methoxylation can be observed only in higher concentrations of acid. The alkylation of pyridine-2-carboxamide was indicated at only four position.

The aim of this work was to study the photostability of *N*-alkyl and *N,N*-dialkylpyridine-3-carboxamides and *N*-alkyl and *N,N*-dialkylpyridine-2-carboxamides: *N*-dodecylpyridine-3-carboxamide **1**, *N*-(2-ethylhexyl)pyridine-3-carboxamide **2**, *N,N*-dihexylpyridine-3-carboxamide **3**, *N,N*-dibutylpyridine-3-carboxamide **4**, *N*-dodecylpyridine-2-carboxamide **5**, *N*-(2-ethylhexyl)pyridine-2-carboxamide **6** and *N,N*-dihexylpyridine-2-carboxamide **7**, as the model extractants of copper from chloride media. The research was carried out in organic solvent (toluene, octane and a mixture of octane–toluene), using UV–vis and vis radiation. The influence of water, hydrochloric acid or air and the effect of the copper(II) ion on the stability of the amides under light exposure were measured.

2. Experimental

Synthesis of pyridine-3 (and -2)-carboxamides synthesized and characterized as reported previously [4]. A purity of 98–99% for synthesized amides was determined by GC/MS. UV, FT/IR, ^1H and ^{13}C NMR, and MS spectra proved the structure of the obtained compounds.

Complexes of pyridine-3-carboxamides with copper(II) were obtained in an extraction process. Studies were performed at constant extractant concentration equal to $2 \times 10^{-1} \text{ mol L}^{-1}$ in toluene. The phase volume ratio was 1. The compositions of the aqueous phase are given in Table 1. After extraction the concentration of copper complexes in the toluene phase was $5\text{--}9 \times 10^{-3} \text{ mol L}^{-1}$ for Cu1 and Cu3 complexes, and $1\text{--}2 \times 10^{-1} \text{ mol L}^{-1}$ for Cu2 and Cu4 complexes. Vis spectra of copper complexes with amide in toluene: *N*-(2-ethylhexyl)pyridine-3-carboxamide $\lambda_{\text{max}} (\epsilon) = 688 (13.8)$ for Cu1 and Cu3; *N,N*-dihexylpyridine-3-carboxamide $\lambda_{\text{max}} (\epsilon) = 774\text{--}776, \sim 850 \text{ nm} (129)$ for Cu1 and Cu3, 858 (121) for Cu2 and 860 (127) for Cu4; *N,N*-dibutylpyridine-3-carboxamide $\lambda_{\text{max}} (\epsilon) = 788 (137)$ for Cu1 and Cu3, 860 (221) for Cu2 and 868 (285) for Cu4 [5].

Table 1
Compositions of the aqueous phase in the extraction process (extractant concentration: $2 \times 10^{-1} \text{ mol L}^{-1}$ in toluene; the phase volume ratio was 1)

Solution	Concentration (mol L^{-1})	
	LiCl	CuCl ₂
Cu1	4	1×10^{-2}
Cu2	4	1
Cu3	6	1×10^{-2}
Cu4	6	1

2.1. Photodegradation procedure

Photodegradation was carried in the same way as with other derivatives of pyridinecarboxylic acid [12], individual model hydroxyoximes and commercial hydroxyoxime extractants [6–8].

The amides samples, $1 \times 10^{-3} \text{ mol L}^{-1}$ in octane, toluene and a mixture of octane–toluene (4:1, v/v) were exposed in a Heraeus photoreactor of 120 mL volume, containing a mercury medium pressure lamp TQ 150 W (Heraeus) and optical filter (quartz or duran glass). The lamp was positioned within the inner part of the photoreactor and cooling water was circulated through a Pyrex jacket surrounding the tube. The quantum yield of the lamp in the photoreactor was $7.86 \times 10^{-5} \text{ Einstein dm}^{-3} \text{ min}^{-1}$. In some experiments, water or hydrochloric acid (4 mol L^{-1}) was also added to 5% of volume to the solutions of octane–toluene or toluene. The solutions were irradiated under bubbling argon or air with the stationary flow of $2 \text{ cm}^3 \text{ min}^{-1}$ at $20\text{--}23 \text{ }^\circ\text{C}$.

Analyses of solutions after light exposure were done using a HPLC/UV with a diode array detector. For the identification of the photoproducts the HPLC/MS technique was also applied using a Waters–Micromass HPLC with an electrospray ionization detector.

The toluene solutions of copper complexes of pyridine-3-carboxamide, Cu1–Cu4 ($1 \times 10^{-3} \text{ mol L}^{-1}$ of ligand concentration) were exposed for 30–240 min in the same manner as amides. The content of the amide in the organic phase after photodegradation was measured using the HPLC technique. Copper stripping was carried out with water, and the content of the extractant in the toluene phase was measured.

3. Results and discussion

The obtained results of photodegradation of the pyridinecarboxamides in octane, toluene, an octane–toluene solution and with 5% (v/v) water or hydrochloric acid in toluene or an octane–toluene solution, indicated that all the tested amides degraded under exposure to UV–vis light. The least degree of photodegradation of *N*-dodecylpyridine-3-carboxamide is observed in toluene solutions, slightly faster photodegradation occurred in the mixture of octane–toluene and in the octane solu-

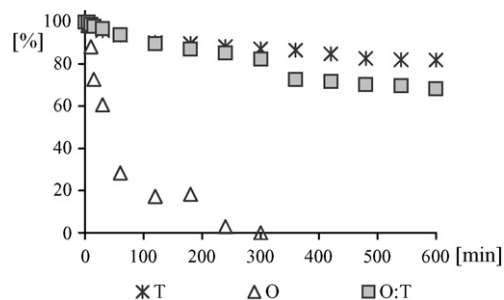


Fig. 1. Relative contents of non-degraded *N*-dodecylpyridine-3-carboxamide dissolved in octane O, toluene T and an octane–toluene solution O:T during exposition of UV–vis light in an argon atmosphere.

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