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# Aromatic acid chlorides dosage with N-acyl-aminoacids in aprotic solvents by a spectrophotometric method

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#### ABSTRACT

The proposed method consists essentially in the treatment of an aromatic acid chloride solution with certain amounts of N-acyl-aminoacid as reagent. The mechanism of the colored chemical reaction is described here and the concentration of the aromatic acid chloride is determined on the basis of Bouguer–Lambert–Beer law. The results are discussed having in view the electrostatic interactions in the liquid solution in which the reaction takes place. The proposed method offers a high sensitivity, accuracy, easiness and quickness of the operations.

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# 1. Introduction

The methods applied for acid chlorides determination do not take into consideration two functional components namely free chlorhidric acid and R-COOH.

In the majority of cases, R-COOH has an interference which is either hidden [1], or determined as an acid chloride by titration with Natrium acetate [2], or Natrium methoxide [3,4], or by precipitation with  $AgNO_3$  [5,6]. The chlorides of the fatty acid with long chains are treated with ammonium and then the halogenated acid is determined by titration [7–11]. The quantitative analyses by titration, hydrolysis, or precipitation are described in the articles mentioned above.

In order to avoid the difficulties which could appear because of the methods described above when acid chlorides are dissolved, Yardimici and Ozaltin [12] have elaborated a spectrophotometric method based on the transformation of the acid chlorides into ferric-hydroxamates in which the reaction medium becomes colored in red-purple.

Due to the hydroxamic acids which appear in alcoholic solution of hydroxylamine (1 mol water/1 mL reactant) the resulted chlorhidric acid can interact with water or with alcohol. This fact can induce significant errors ( $\approx 10\%$ ).

In this paper a new method for the acid chlorides dosage is discussed. It is more advantageous as regards the duration, simplicity and accuracy of the results.

The proposed method is essentially based on the spectrophotometric determination of a colored anion of  $2-(p-nitrophenyl)-4-R-\Delta^2-$ 

\* Corresponding author. *E-mail address*: moise\_mihaela82@yahoo.com (M. Mihaela). oxazolinone-5 which is obtained by reaction between acid chlorides of the one of the following reactants: N-(p-nitrobenzoyl)-L-phenylglicine or N-(p-nitrobenzoyl)-L-phenylalanine [13].

### 2. Experimental part

The proposed method consists in the treatment of an acid chloride in anhydric solvents by a given amount of N-acyl-aminoacid and three-ethyl-amine, followed by a spectral analysis and by comparing the results with the standard curves.

The reactants were prepared from 1.5 g of N-acyl-aminoacid and 2.08 g three-ethyl-amine in 25 mL dimethylformamide (DMF), dichloromethane chloroform, acetone and dioxane.

Separately, the acid chloride solutions in anhydre solvents (chloroform and acetone) with a concentration of  $(0.5-4.0)10^{-3}$  mol/L were prepared and then they were added to each N-acyl-aminoacid solution. A red-violet coloration was obtained. The samples must be immediately analyzed because their color persists only for 2–3 min. Then, the color progressively disappears in a short interval of time [14–19].

The standard curves were obtained at fixed molar concentrations, as it results from Fig. 1. Spectral measurements were made at Specord UV VIS spectrophotometer with a data acquisition system.

# 3. Results and discussions

Three acid chlorines from o-, m-, and p-nitro benzoic acids were used in spectrophotometric measurements [20]. The graphs from Fig. 1 indicate the applicability of Bouguer–Lambert–Beer law for the spectral data.

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Fig. 1. Optical dependence of absorbance versus concentration for conpounds III and IV (ortho, para, and meta).

By measuring the absorbance in the maximum of the electronic absorption band of chlorhidric acid having a known concentration, between 0.3 and  $0.7 \cdot 10^{-3}$  mol/L, and comparing the results with those obtained from the standard curves, the maxima of errors were the following: ortho-nitro benzoic acid chloride  $-\pm 0.11\%$ ; metanitro benzoic acid chloride  $-\pm 0.20\%$ ; para-nitro benzoic acid chloride  $-\pm 0.09\%$  (Table 1).

The wavelength in the maximum of the electronic absorption band of the chloral-anion was 522 nm for 2-(p-nitrophenyl)-4-phenyl- $\Delta^2$ -oxazolone-5 and 485 nm for 2-(p-nitrophenyl)-4-benzyl- $\Delta^2$ -oxazolone-5, respectively.

In basic medium, the reactions in the studied mixture lead to two oxazolones and depend on the solvent nature (Fig. 2).

Let us consider that the apparition of the mixed anhydrides ( $A_{I, II}$ ) correspond to a  $SN_2$  mechanisms and it is favored by the electron withdrawing effect of  $-NO_2$  substitute, on the carbon belonging to carboxylic substitute from N-acyl-aminoacids I and II. On the other hand the carboxylic group activation produced by the -p-nitrobenzoyl rest, as well as the decrease in the strength of the hydrogen chemical bond in the amyl substitute caused by the nitrophenyl rest could explain the rapid cyclization of the mixed anhydrides  $A_{I, II}$  to the oxazolones III and IV, the anions  $B_{I, II}$  being more in rapport to the anhydrides.

Concerning the apparition of the blue coloration, we think it is due to the conjugated ion formed in the triethylamine presence in the studied system, favored by the presence of three strong electron withdrawing groups in the oxazolones' molecules (-C O; -C N;  $-NO_2$ ). In these conditions, the hydrogen atom from  $\alpha$  position is more activated (Fig. 3).

#### 4. Conclusions

A new spectrophotometric method for the analysis of the aromatic acid chlorides was advanced by using two organic reagents: N-(para-nitrobenzoyl)-L-phenylglycine and N-(para-nitrobenzoyl)-L-phenylalanine.

The possibility of dosing the acid halides in the presence of HCl and R-COOH in the same solvent where they have been obtained avoids



I, III  $R = -C_6H_5$ ; II, IV  $R = -H_2C-C_6H_5$ ; A, B  $R' = -C_6H_4-NO_2(o,m,p)$ 

I  $R = -C_6H_5$ ; N-(p-nitrobenzoyl)-L-phenylglycine

- II  $R = -H_2C C_6H_5$ ; N-(p-nitrobenzoyl)-L-phenylalanine
- III  $R = -C_6H_5$ ; 2-(p-nitrophenyl)-4-phenyl-D<sup>2</sup>-oxazolinone-5
- $IV R = -H_2C-C_6H_5$ ; 2-(p-nitrophenyl)-4-benzyl-D<sup>2</sup>-oxazolinone-5

Fig. 2. Reaction mechanism for obtaining oxazolones.

#### Table 1 Results for fits of lines (1) from Fig. 1.

Substance	$A \pm \Delta A$	$B \pm \Delta B(L/mol)$	R	SD	Ν	Р
III (o)	$-0.0038 \pm 0.0023$	$0.2447 \pm 0.0009$	0.99	0.0037	9	0.0001
III (p)	$0.0009 \pm 0.0003$	$0.1807 \pm 0.0012$	0.99	0.0046	9	0.0001
III (m)	$0.0022 \pm 0.0003$	$0.12167 \pm 0.0013$	0.99	0.0051	9	0.0001
IV (o)	$0.0022 \pm 0.0035$	$0.1533 \pm 0.0015$	0.99	0.0056	9	0.0001
IV (p)	$-5.5 \cdot 10^{-17} \pm 3.8 \cdot 10^{-17}$	$0.2 \pm 1.63 \cdot 10^{-17}$	1	$6.29 \cdot 10^{-17}$	9	0.0001
IV (m)	$0\pm 0$	$0.22\pm0$	1	0	9	0.0001





their rather difficult separation with inherent decomposition and losses by vaporization.

The anhydrous solvent also prevents from the hydrolysis reaction which could generate significant errors.

A mechanism is advanced for the color reaction on which this method is based.

This method shows several advantages over the other methods known for the analysis of acid halides. Thus, it offers higher sensitivity, accuracy, easiness and guickness of the operation.

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