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STUDY OF MODEL REACTION OF SYNTHESIS OF *n*-BUTYL ACETATE USING IR SPECTROSCOPY IN SOLUTION

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ABSTRACT

FT-IR spectroscopy is an absorption method, used to obtain the infrared spectrum of a chemical compound in a sample in order to monitor specific functional groups in organic and inorganic compounds. Herein, the ability of this technique to be used for on-time monitoring of a model chemical reaction is demonstrated. Every chemical reaction is characterized by specific kinetic profile, especially when a reversible reaction as esterification has to be realized. The selection of an appropriate, easy to be applied tracking technique is an important moment in the industry. N-butyl acetate can be obtained by the esterification of n-butan-1-ol and acetic acid. The main purpose of the presented work is to study the kinetics of the model reaction of n-butyl acetate synthesis showing the ability of FT-IR technique in solution to be used. Process of on-time monitoring can help to study the external factors which influence on the both right and reversed reaction in order to obtain the best yield of aimed product. The obtained results showed that FT-IR technique could be used as an easy to be applied for on-time monitoring of esterification reaction technique and the reaction reaches equilibrium in the 90th minute. Otherwise, a yield of 100 % is observed after one hour and half since the beginning of the reaction.

Keywords: *IR spectroscopy in solution, esterification reaction, n-butyl acetate.*

INTRODUCTION

Esters are compounds with a variety of applications in practice and mostly commonly used as fragrances and found in essential oils and pheromones [1]. For example, ethyl ethanoate is found in pineapples, pentyl butanoate in apricots, ethyl methanoate in rum, and octyl ethanoate in oranges [2]. In addition, esters are used as prodrugs. Coupling the acid carboxylic group of a nonsteroidal anti-inflammatory agent with alcohols (esterification) leads to a reduction in the gastrointestinal side effects of drugs.

Esterification reaction is a process of combining of an alcohol with an acid. Due to reversibility of the reaction the ester yield is limited unless one of the products is removed from the reaction system during the reaction [3]. This problem has been encountered during the synthesis of butyl acetate. This substance is one of the most popular fruit flavors and widely used in food production [4]. In U.S. Environmental Protection Agency (EPA) chemical and products databases are mentioned more than 70 industrial and chemical uses of butyl acetate [5].

Several instrumental and analytical methods are largely used in practice for tracking of substrates to products transformation. Every method has own features and could find appropriate application. It is not easy to find the most convenient method for each chemical reaction. The choice of the method depends on the kinetic of the reaction and specific features of the reactants, sample's type and required detection level. Herein, in order to do a quantitative analysis of the model esterification reaction between butyl alcohol and acetic acid the FT-IR spectroscopy in solution was chosen. The technique is based on the ability of a sample to absorb IR radiation. However, the ability to monitor the reaction during process of realization is very valuable for industrial application. For the need of quantitative analysis, the intensity of the absorption bonds is used to determine the concentration of reaction components [6, 7].

The aim of the presented work was to monitor the dynamics of model reactions by monitoring changes of the characteristic bands of transforming groups directly in liquid phase using IR spectroscopy.

Tracking the kinetics and dynamics of chemical transformations by FT-IR method in solution is a rapid innovative method. This method is not convenient to all type of chemical reaction that why a several conditions should be taken in consideration:

- the selection of reactants and solvents in which the reaction is carried out, so that they do not mask the spectra of our product in the sample;
- to select a suitable solvent in accordance with the KBr cuvette used during the analysis.

EXPERIMENTAL

The reaction was carried out under standard esterification conditions, namely an excess of the target alcohol *n*-butan-1-ol in an acidic medium (Fig. 1).

The model reaction of esterification was monitored as follows:

- 200 μL samples of the reaction mixture were taken in 0, 30, 60, 90, 150, 210 min.
- The samples are diluted in 4 mL of pure solvent dichloromethane (DCM).
- The obtained solution was dried with Na_2SO_4 and the IR spectrum is recorded in the interval 2000 cm^{-1} - 1500 cm^{-1} with 2 cm^{-1} resolution.

All reactions were monitored on "VARIAN" 660 IR FT-IR Spectrometer equipped with KBr SmartSeal Liquid Transmission Cell with following parameters: pathlength 0.15 mm and volume 0.022 mL in the Central Laboratory for Scientific Investigations of University of Chemical Technology and Metallurgy, Sofia.

The used reagents were supplied by Valerus (Bulgaria) and were used without any preliminary treatment.

RESULTS AND DISCUSSION

Taking into account the available data related to the spectrum of target functional group FT-IR allows to detect the sample kinetic or the transformation of the alcohol in ester.

The carbonyl (C=O) stretch is one of the most distinctive bands in the IR spectrum. It can be found as a strong peak at 1640 cm^{-1} - 1820 cm^{-1}. The absorption ranges for the various carbonyl-containing functional groups overlap significantly (Table 1), so it is difficult to make a definite identification of the functional group based solely on the position of the carbonyl peak [8].

As it is mentioned above the choice of a convenient

Table 1. Carbonyl Compounds Functional Group and their absorption intensity wavelengths [8].

Compound group	Absorption Intensity wavelength cm^{-1}
Aldehyde (RCHO)	1720 - 1740
Ketone (RCOR’)	1705 - 1750
Ester (RCO_2R')	1735 - 1750
Carboxylic acid (RCO_2H)	1700 - 1725

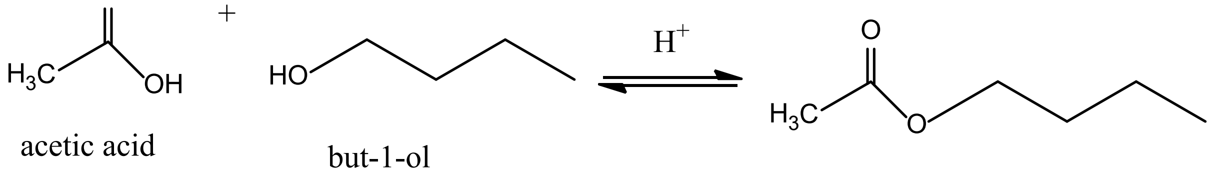

Fig. 1. Reaction scheme of the esterification between but-1-ol and acetic acid.

solvent is an important step in the study of transformation reactions in solution using FT-IR. In this experiment DCM was chosen as a solvent for several reasons:

- the ability to dissolve a wide range of organic compounds;
- it does not mask the bands of C=O (ester);
- it does not react with alkaline halides, such as commercially available cuvettes for recording IR spectra in solution;
- it allows monitoring by IR in solution.

The collected spectra at 0, 30, 60, 90, 150, 210 min are presented in Fig.2.

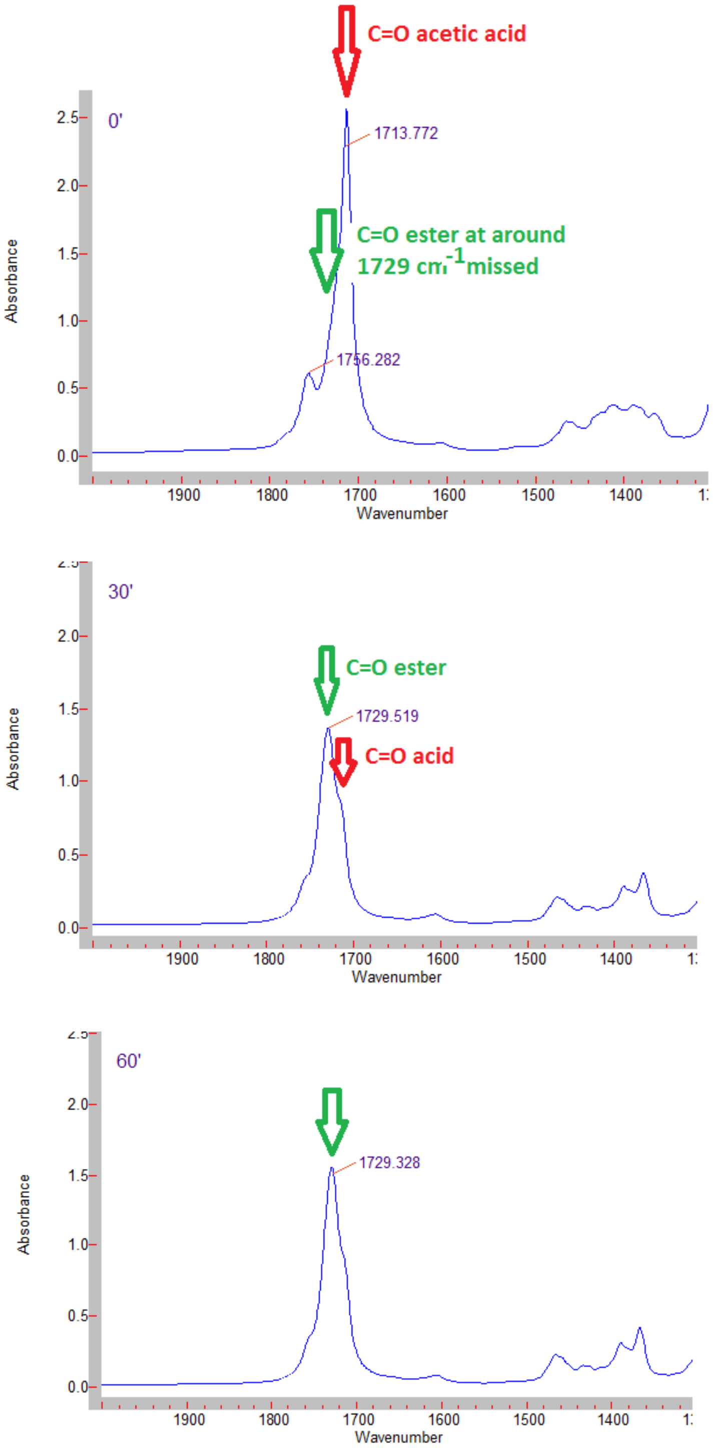

Fig. 2. IR spectra at time of monitored reaction - *continued*.

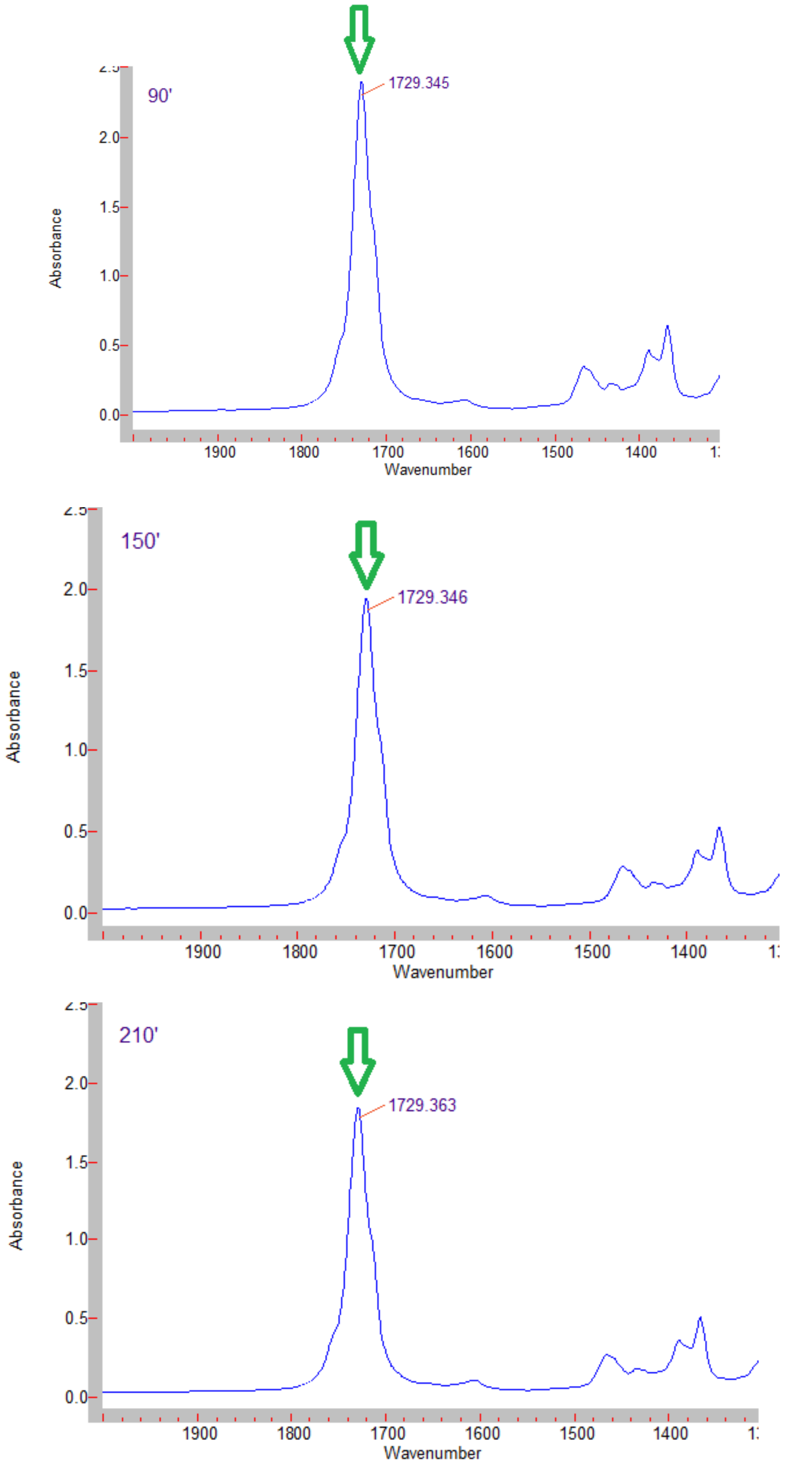

Fig. 2. IR spectra at time of monitored reaction - *continued*.

From the obtained data we can observe almost 100 % depletion of the free C=O (acetic acid) group, i.e. almost 100 % transformation of the acid in ester within 90 min of the reaction. The augmentation in the area of the valence band of the C = O (ester) group at 1729 cm^{-1} indicates an augmentation in the concentration of *n*-butyl acetate in the sample. The diminution in the intensity of absorption after 100 % yield at 150 min

Table 2. Data for the dynamics of the esterification reaction in the solution.

	Changing band	
	Band for C=O ester [~1729 cm^{-1}]	
	area	yield [%]
0	0	0
30	42785	60.5
60	50691	71.6
90	70766	100
150	57755	81.6
210	54559	77.1

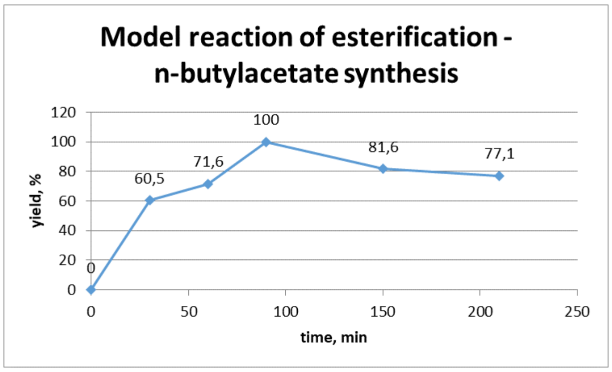

Fig. 3. Dynamic transformation in the model esterification reaction in the solution.

confirms the diminution in the ester's concentration, due to the presence of water as an esterification's product, which moves the reaction to the opposite direction. The dynamic of the reaction is summarized in Table 2 and presented in Fig. 3.

It is clear from the obtained FT-IR data that the esterification reaction under the selected conditions takes place completely in 90 min.

CONCLUSIONS

The obtained data show that the maximum yield of the target ester is observed at 90 minutes of the reaction. The presence of water allows a secondary hydrolysis reaction to begin, which is evident from the decreasing area of the observed peak for C=O at 1729 cm^{-1}. A possible alternative for pulling the reaction towards obtaining the target ester in high yield is to de-distillate the resulting ester from the reaction mixture to prevent the unwanted secondary hydrolysis reaction.

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