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Microwave inducted thermal gradients in solventless reaction systems

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Keywords

Microwave irradiation, benzofuran, solventless solid-liquid reaction

Abstract

Development of thermal heterogeneity in microwave irradiated solventless solid-liquid reaction mixtures has been studied.

Introduction

Microwave heating is very efficient method for improving the yield of many organic transformations. Many authors suppose that it is a result of specific microwave interaction with reagents [1-2]. In homogenous chemical systems there are a possibilities of creating thermal homogeneity (mechanical stirring, boiling chips) and investigation of non-thermal microwave influence are justifiable. In the case of heterogeneous conditions there are thermal gradients confirmed by both theoretical calculation [3] and experimental results (in the case of gas-phase transformations on the solid catalyst [4]).

In the present study, we decided to apply the microwave protocol to investigate the reaction of salicylaldehyde **(1)** with ethyl ester of chloroacetic acid **(2)** under a solid-liquid PTC conditions in the presence of K_2CO_3 and tetrabutylammonium bromide (TBAB) as a catalyst. The reaction results in the formation (2-formyl-phenoxy)-acetic acid ethyl ester **(3)** and, after the further intermolecular condensation of **(3)**, in benzofuran-2-carboxylic acid ethyl ester **(4)**, which is the final product (Figure 1) [5].

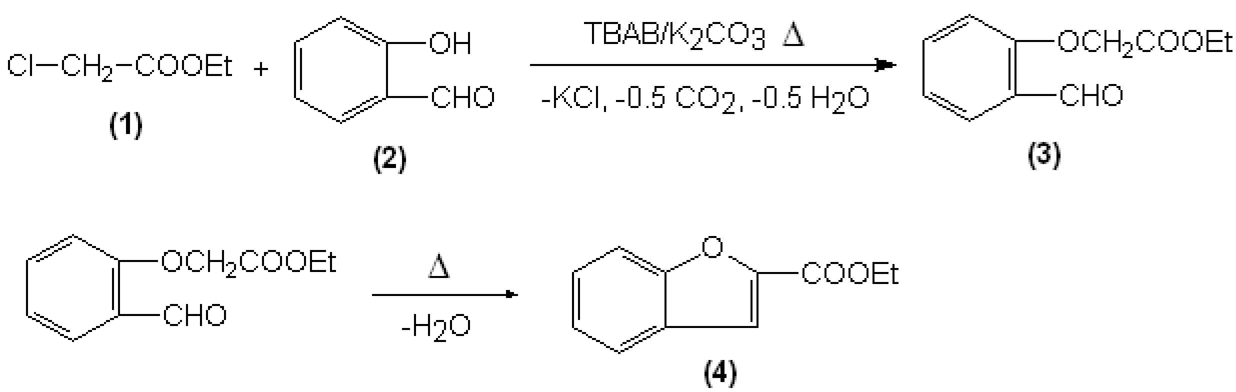

Figure 1. Preparation of benzofuran-2-carboxylic acid ethyl ester

Experimental

In a typical experiment, the reactions were carried out by simple mixing of salicylaldehyde (0.61g/5mmol) and chloroacetic acid ethyl ester (1.22g/10mmol). The mixture was than adsorbed on potassium carbonate (2.70g/20mmol), and irradiated 3 minutes in an open quarz vessel (4 cm of diameter) in a monomode microwave reactor (SynthWave402, Prolabo, moximum power 300W). To control the reaction temperature during experiments fibreoptical sensor (ReFlex, Nortech) and thermovision camera (V-20, VigoSystem) were used. The reaction mixture was extracted with 20 ml of acetone and analysed by means of gas chromatography (5890 HP) coupled with a mass detection (5971 HP).

Results and discussion

As a result we can state that the existence of significant thermal gradients in the reaction mixture was observed. Figure 2 shows the photography of the reaction mixture surface after microwave experiment. There are dark and light areas, indicating different reaction product distributions (local selectivity), proved by analysis of samples taken from places P1, P2 and P3. Additionally, based on thermovision measurements (Figure 3), we can affirm that maximal temperature estimated on the surface of the reaction mixture was about 200^{o}C, and minimal 60^{o}C. It seems to be an interesting phenomena especially in such small reaction mass. Described thermal gradient is bigger than 100^{o}C and origins by strong interactions of microwave irradiation, with polar reagents.

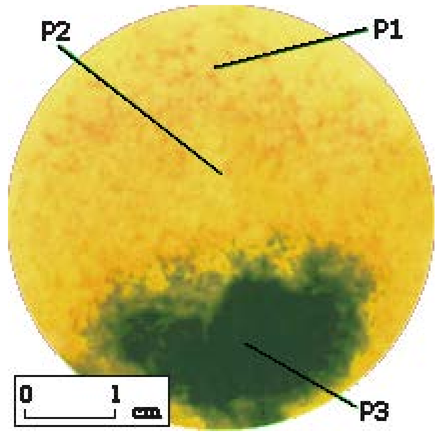

Figure 2. Photography of the surface of the reaction mixture after reaction in microwave condition

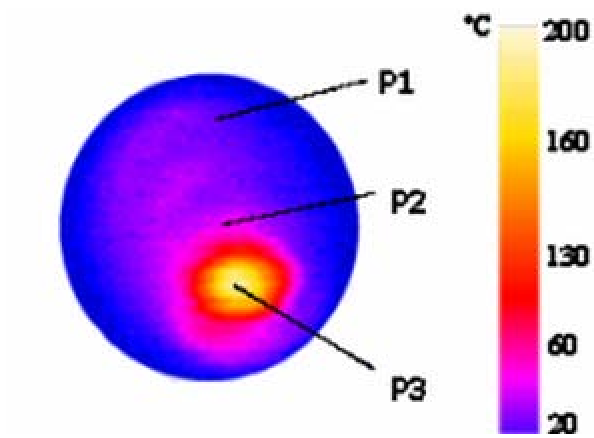

Figure 3. Thermovision photography of the surface of the reaction mixture during microwave experiment

Table 1. Local composition of the reaction mixture (Figure 2)

Sample	**(3)** %	**(4)** %
P1	100	0
P2	55	45
P3	0	100

As a conclusion we can say, that in the case of solvent free solid-liquid reaction, carried out in microwave field, there is a possibility to form high thermal gradients inside reaction mixture what may lead to higher conversions. Therefore, before considering the increase of reaction rates by special microwave effects (*thermal* or *non-thermal*), first, we need to consider all the factors that might influence chemical reactions under microwave conditions like a reaction mechanism and temperature profiles (gradients).

Literature

1. Microwaves in Organic Synthesis, A. Loupy, (Ed.), Wiley-VCH, Weinheim, 2002.

2. C. O. Kappe, A. Stadler, Microwave in Organic and Medicinal Chemistry, Wiley-VCH, Weinheim, 2005.
3. M.E.C. Oliveira, A.S. Franca, Int. Comm. Heat Mass Transfer, 2000, 27, 527; J. Clemens, C. Saltiel, Int. J. Heat Mass Transfer, 1996, 39, 1665.
4. X. Zhang, D.O. Hayward, D.M.P. Mingos, Chem. Commun., 1999, 975
5. D. Bogdal, M. Warzala, Tetrahedron, 2000, 56, 8769