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# Microwave induced thermal gradients in solventless reaction systems

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**Abstract**—Development of thermal heterogeneity under microwave irradiation for solventless solid–liquid phase-transfer catalytic (PTC) reactions has been studied by means of a thermovision camera and fiber-optics thermometer.

## 1. Introduction

Recently, microwave irradiation has been found to be a very efficient tool to improve yields of a great number of chemical transformations.[1–3] Many authors suppose that it might be a result of specific microwave interaction with reagents on molecular scale when the reaction system's polarity is increased from a ground state to a transition state[4] or on macromolecular scale, which in turn influences yield[5] as well as selectivity.[6] Most recent critical reviews concerned with these effects were published by Perreux and Loupy,[4] Nuchter et al.,[5] and de la Hoz et al.[6]

The most successful examples of microwave applications were found to be related to the use of heterogeneous solvent-free systems, in which microwaves interact directly with reagents and, therefore, can more efficiently drive chemical reactions. The possible accelerations of such reactions are expected to be optimal since they are not moderate or impeded by solvents.[7] On the other hand, in diluted homogenous chemical systems in which it is possible to obtain a good thermal homogeneity by use of an effective mechanical stirring or/and boiling chips, it was proved that acceleration of microwave-assisted reactions was rather negligible;[8,9] however, it could be also dependent on the mechanism of the reaction.[10]

Temperature measurement during microwave irradiation of materials is the major problem in microwave-enhanced processing of materials. However, there is a general agreement that the application of fiber-optics thermometers is the only reliable way to determine temperature under microwave conditions; using a thermovision camera, we reported that the application of a pyrometer and fiber-optics thermometer did not give correct values while high temperature gradients were developed within reaction mixtures.[11–13] For example, it was shown that heterogeneous support like Magtrieve, which is a strong microwave absorber, could reach higher temperature than the boiling point of a solvent applied in the synthesis, but a pyrometer and fiber-optics thermometer did not show this effect.[11,12] In another example, in the case of viscous homogenous reaction media like epoxy resins, a thermovision camera showed high temperature gradients on the surface of the reaction mixtures. Since in some parts of the sample local temperatures under microwave irradiation can be different, pyrometers as well as fiber-optics thermometers gave only information about the local temperatures but bulk temperature of the reaction mixture was hard to estimate.[13]

## 2. Results and discussion

In the present study, we decided to apply the microwave protocol to investigate the reaction of salicylaldehyde with ethyl ester of chloroacetic acid under solid–liquid PTC conditions in the presence of $K_2CO_3$ and tetrabutylammonium bromide (TBAB) as a catalyst. The reaction resulted in the formation of (2-formylphenoxy)acetic acid ethyl ester (**1**), which after further intermolecular condensation gave benzofuran-2-carboxylic acid ethyl ester (**2**)—the final product (Scheme 1).

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*Keywords*: Microwave irradiation; Benzofuran; Solventless solid–liquid reaction.

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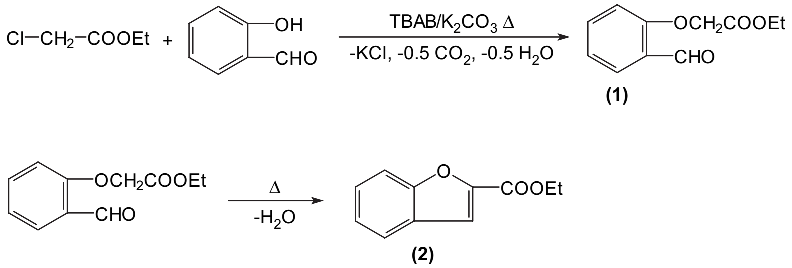

**Scheme 1**. Preparation of benzofuran-2-carboxylic acid ethyl ester.

This reaction was chosen as the test reaction because in our previous study we had found that it was an effective way for the synthesis of a number of benzofuran derivatives.[14] When the reaction was run with the same reaction temperature profiles under both conventional (oil bath) and microwave conditions, different distributions of the intermediate (**1**) and final product (**2**) were determined (Table 1). It is worth stressing that the product distribution was much strongly affected by the microwaves, and the yield of **2** was higher in comparison with conventional experiments when the reaction was run at lower temperatures; for example, 85 °C (Table 1, entries 4 and 5) versus 110 °C (Table 1, entries 2 and 3). Thus, in order to observe the influence of microwave irradiation on chemical reactions if the yields were high under both microwave and conventional conditions it was required not to increase but decrease the reaction temperatures, which have been shown in previous reports.[15] In our case, it allowed finding a temperature range where yields or/and product distributions were different for both protocols (Table 1). Furthermore, the addition of a small amount of polar or non-polar solvents also influences the product distribution. In this case, two solvents were applied: one capable of strongly coupling and the second not coupling with microwaves, i.e., ethanol and cyclohexane, respectively. The addition of ethanol strongly shifted the product distribution toward the final product (**2**), whereas the addition of cyclohexane resulted in much lower yield of **2**.[16] The extensive discussion on the influence of reaction medium, reaction mechanism, temperature, temperature measurement method, and stirring on the reaction yield and selectivity under microwave irradiation in comparison with conventional thermal heating can be found in the literature.[17,18]

For the purpose of the present investigation on thermal gradients in heterogeneous systems in which the development of such gradients has been confirmed by both theoretical calculations as well as experimental results,[19–21] we decided to repeat our previous experiments[14] under slightly modified conditions so that it was possible to use a thermovision camera. The development of a temperature gradient (superheating) within a cross-section of alumina within a Petri dish has been already presented by means of a thermovision camera. Then kinetic calculations of a theoretical reaction indicated that the yield of this reaction might be higher because of the development of temperature gradients under microwave irradiation.[20] In this paper, we were able to prove these conclusions experimentally.

First of all, we have observed that crude compounds **1** and **2** adsorbed on the surface of $K_2CO_3$ gave different colors (i.e., yellow (**1**) and brown (**2**)), which were utmost of importance and permitted to visually follow the progress of the reaction (Figs. 1 and 2). At the same time, temperature of the reaction mixtures and temperature of the surface were determined by fiber-optics thermometer (ReFlex, Nortech) and thermovision camera (V-20, VigoSystem), respectively. The results of the experiments under conventional conditions that were run in order to find optimal conditions for microwave experiments are shown in Table 2. Obviously, the reactions were carried out without a mechanical stirring of the reaction mixtures in order to monitor them with the thermovision camera.

**Table 1**. The distribution of the intermediate (**1**) and the final product (**2**) in the synthesis of benzo[*b*]furans under both conventional (Δ) and microwave (MW) conditions

| No. | Temperature (°C) | Time (min) | Solvent (ml) | Yield (%) | |
|---|---|---|---|---|---|
| | | | | **1** | **2** |
| 1 | 110 | 10/MW | — | 12 | 66 |
| 2 | 110 | 20/MW | — | — | 100 |
| 3 | 110 | 20/Δ | — | 4 | 96 |
| 4 | 85 | 20/MW | — | 15 | 85 |
| 5 | 85 | 20/Δ | — | 90 | 10 |
| 6 | 85 | 30/MW | Cyclohexane (1.5) | 62 | 38 |
| 7 | 85 | 30/MW | EtOH (100%) (1.5) | 0 | 100 |
| 8 | 85 | 30/MW | EtOH (96%) (1.5) | 0 | 100 |
| 9 | 85 | 30/Δ | EtOH (100%) (1.5) | 47 | 53 |

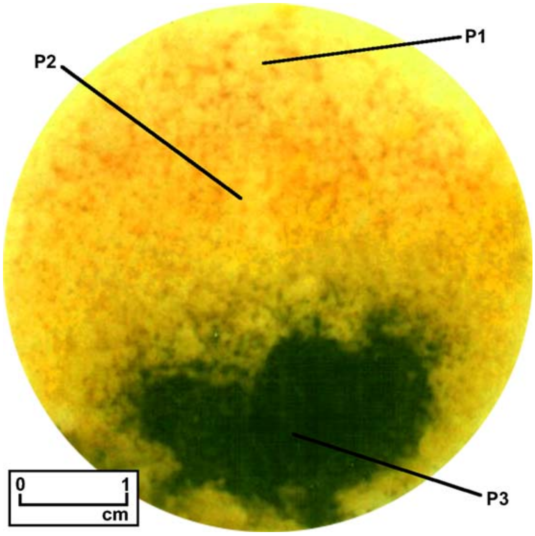

**Figure 1**. Photograph of the surface of the reaction mixture (Table 3, entry 1).

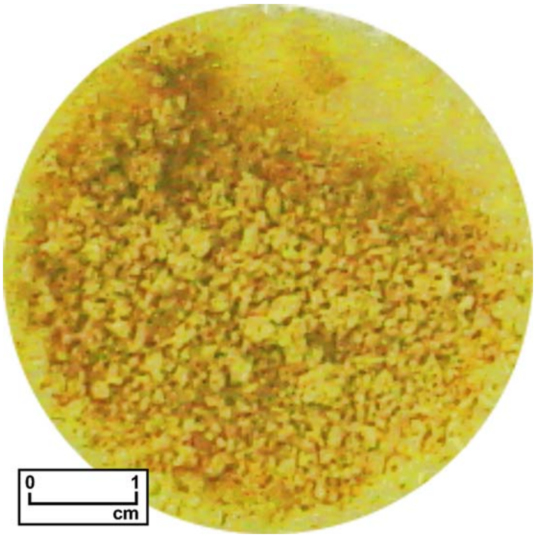

**Figure 2**. Photograph of the surface of the reaction mixture (Table 3, entry 2).

**Table 2**. The influence of temperature on the product selectivity of **1** and **2** in the synthesis of benzo[*b*]furans under conventional conditions (5 min)

| No. | Temperature (°C) | Catalyst (0.5 mmol) | Selectivity[a] (%) | |
|---|---|---|---|---|
| | | | **1** | **2** |
| 1 | 70 | TBAB | 100 | 0 |
| 2 | 95 | TBAB | 48 | 52 |
| 3 | 115 | TBAB | 12 | 88 |
| 4 | 135 | TBAB | 0 | 100 |
| 5 | 145 | TBAB | 0 | 100 |
| 6 | 95 | — | 100 | 0 |
| 7 | 110 | — | 74 | 26 |
| 8 | 150 | — | 11 | 89 |
| 9 | 80[b] | TBAB | 0 | 0 |
| 10 | 80[b] | — | 0 | 0 |
| 11 | 90[c] | TBAB | 0 | 0 |
| 12 | 90[c] | — | 0 | 0 |
| 13 | 110[d] | TBAB | 3 | 97 |
| 14 | 85[d] | TBAB | 71 | 29 |

[a] The reaction's selectivity is determined by GC/MS.
[b] $Al_2O_3$ was used instead of $K_2CO_3$.
[c] Without any solid support.
[d] The reaction time was 20 min.

However, the addition of the catalyst (i.e., TBAB) strongly increased the yield of the final product (**2**) (Table 2, entries 1–5), it was also possible to carry out the reaction without the catalyst at elevated temperatures (Table 2, entries 6–8). Moreover, the use of TBAB resulted in the release of volatile products of its decomposition upon the surface of the reaction mixtures that in turn strongly influenced the temperature measurements by means of the thermovision camera (i.e., release of any vapor within the reaction vessel immediately leads to disability of the thermovision camera).

It was also found that the reaction did not occur when $K_2CO_3$ was substituted with another commonly used mineral support, i.e., $Al_2O_3$ or when the reagents were applied without any support (Table 2, entries 9 and 10, respectively). Finally, for the purpose of microwave investigation with the thermovision camera it was decided to carry out the reaction on $K_2CO_3$ support at 110 °C without the catalyst. The results of the microwave experiments are presented in Table 3.

**Table 3**. Average[a] reaction selectivity depending on experimental mode

| No. | Selectivity[a] (%) | | Description |
|---|---|---|---|
| | **1** | **2** | |
| 1 | 33 | 67 | No stirring |
| 2 | 70 | 30 | Vessel rotation |
| 3 | 84 | 16 | Vessel rotation and stirring |
| 4 | 100 | 0 | No stirring, addition of 6 ml of decane |
| 5 | 67 | 33 | No stirring, vessel rotation |
| 6 | 77 | 23 | No stirring, vessel rotation |

[a] Average selectivity determined by GC/MS from entire reaction mixture. All microwave experiments were carried out in the same condition: maximal microwave power 240 W, maximal temperature 110 °C.

The first three experiments (Table 3, entries 1–3) were carried out in order to check the influence of the rotation of the reaction vessels and stirring of the reaction mixture on process selectivity. In the case of the first experiment (entry 1), the reaction mixture was placed in the microwave reactor without any rotation of the reaction vessel. In the second case (entry 2), there was only applied a vessel rotation, while in the third case (entry 3) there was used the vessel rotation and mechanical stirring by immobilizing the quartz spatula inside the reaction vessel.

At the beginning, the development of thermal gradients during microwave experiments on the surface of reaction mixtures was confirmed visually, i.e., it was possible to observe the formation of brown spots in all the places where the compound **1** was converted to **2** (Figs. 1 and 2). These observations were later proved by the analysis of the samples taken from different places from the surface of the reaction mixtures. Also, thermal gradients were revealed by means of the thermovision camera, which detected strong temperature increase in the central part (on the side of the microwave waveguide in the reactor) of the reaction mixture in comparison to outer regions (Fig. 4).

Eventually, the existence of thermal gradient was proved by the quantitative analysis by taking samples from different places of reaction mixtures that exhibited different temperatures during the reactions (Figs. 1 and 4, entries P1, P2, and P3). The results are summarized in Table 4. It can be seen that the highest conversion of **1** to **2** was found for the sample P3, which exhibited the highest temperature (ca. 200 °C) during the microwave experiment (Table 4, entry 3). Then the conversions of **1** to **2** 45% and 0% were observed for the samples P2 and P1, which gained lower temperatures than P3, i.e., 125 °C (Table 4, entry 2) and 70 °C (Table 4, entry 1), respectively. These results are in good agreement with the experiments under conventional conditions (Table 1), in which it was shown that only the samples that reached higher temperature (more than 150 °C) can give high

**Table 4**. Local composition of the reaction mixture (Figs. 1 and 4)

| Sample | Color | Temperature (°C) | Yield (%) | |
|---|---|---|---|---|
| | | | **1** | **2** |
| P1 | Light | 70 | 100 | 0 |
| P2 | Brown | 125 | 55 | 45 |
| P3 | Dark | 200 | 0 | 100 |

conversion of **1** to **2** (Table 1, entry 8) without a catalyst. For the samples that reached temperatures lower than 100 °C (Table 1, entry 6), no conversion of **1** to **2** was observed at all.

It has been shown that the investigated reaction system is characterized by the strong interaction with microwaves, which results in very high heating rates. Therefore, a lot of heat can be generated within a small amount of the material in a relatively short time (3 min). This behavior leads to overheating and difficulties in proper temperature measurement. The investigation has proved the existence of thermal heterogeneity in microwave irradiated reaction mixtures without rotation, occurring as a result of significant differences in intensity of microwave field in a reactor cavity.

The rotation of the reaction vessel within the microwave cavity decreases substantially the temperature gradient; however, still the regions are characterized by different colors, i.e., different concentrations of **1** and **2** in the reaction mixture (Fig. 2). In fact, the rotation of reaction vessels reduced overheating, the reaction mixture was exposed to more homogenous microwave field, and, in turn, the yield of **2** was lower (Table 3, entry 2) than for the experiments without rotation (Table 3, entry 1) but much closer (i.e., comparable) to the yield of the reaction under conventional conditions (Table 2, entry 7).

The mechanical stirring with a quartz spatula placed within the reaction mixture improved the thermal homogeneity of the reaction mixture to a greater extent than the rotation of the reaction vessels (Table 3, entry 3); the results are comparable to those obtained under conventional conditions (Table 2, entry 7). Although, it is hard to jump to further conclusions since we did not run conventional protocol with the stirring of reaction mixtures, it can be seen (Fig. 3) that the surface of the reaction mixture was more homogenous in comparison with the experiments with vessel rotation (Fig. 2) and, in particular, without rotation (Fig. 1). Two additional experiments (Table 3, entries 5 and 6) were performed in order to observe the repeatability of the microwave protocol and they gave satisfactory results. It was also shown that the addition of an inert liquid, *n*-decane (Table 3, entry 4), which was added in such an amount that it formed 1–2 mm layer over the top of the reaction mixture, improved temperature homogeneity too; however, it was a bit difficult to observe with the thermovision camera and visually, but the fiber-optics thermometer showed the same temperature (i.e., ca. 110 °C) at every region of the reaction mixture.

**Figure 3**. Photograph of the surface of the reaction mixture (Table 3, entry 3).

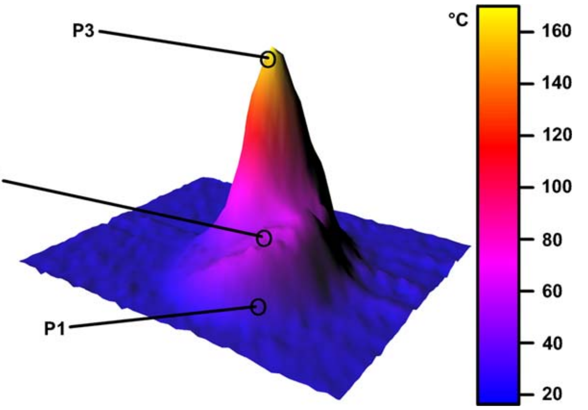

**Figure 4**. Thermovision photograph of the surface of the reaction mixture during the experiment (Table 3, entry 1).

The results presented above are important because one can expect that overall reaction yields given in Table 3 should be similar for all the experiments and do not show significant differences during additional rotation of the vessels and/or stirring of the reaction mixtures. It can be assumed that the overall energy input given by microwaves is similar in all the cases, thus the reaction rate can be different in different regions of the reaction mixture because temperature is different but overall reaction rates should be comparable. In fact, we observed an opposite situation, the increase in temperature homogeneity caused a decrease of the overall reaction yields and made them comparable to those obtained under conventional conditions.

Eventually, Figure 5 illustrates the relation between temperature measured by the fiber-optics thermometer and thermovision camera versus reaction time for the two experiments without and with an inert solvent (Table 3, entries 1 and 4, respectively). In all the cases, temperatures measured by the thermovision camera were lower than those measured by the fiber-optics thermometer. It can be also seen that the temperature differences between the fiber-optics thermometer and thermovision camera were higher for the experiment with the inert solvent (Table 3, entry 4) in comparison with the experiments without the solvent (Table 3, entry 1). It can be explained by the difficulties in temperature measurements by the thermovision camera in the presence of solvent, which was mentioned earlier, as well as heat transfer process of non-polar liquids that proceeds only via conventional heat transport (i.e., thermal conduction) that is slower than microwave heating. Thus, in such a case temperature measurements under microwave irradiation were inaccurate for two possible reasons. First, the rate of heating is so high and measurement devices have some specific thermal inertia during temperature measurements. Second, there

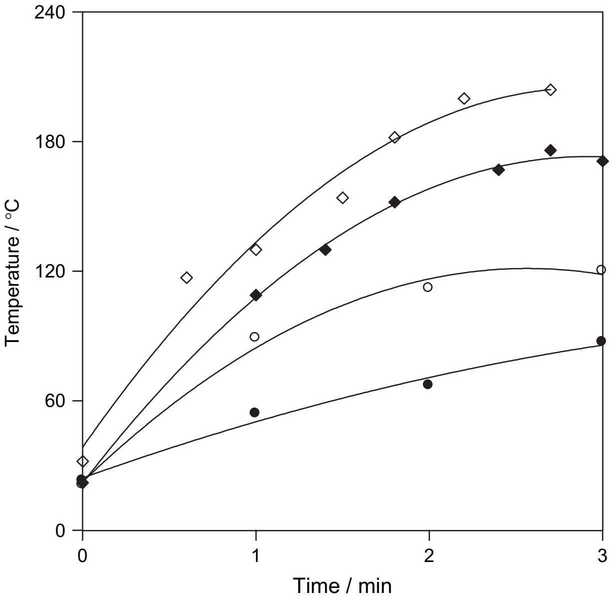

**Figure 5**. Relation between time and temperature, during reaction progress, measured by fiber-optics thermometer in the hot zone—P3 (◇) and shown by thermovision camera as maximal (◆) (Table 3, entry 1). For the sake of comparison two curves were added: temperature measured by the fiber-optics thermometer placed in the position identified as the hot zone (○) and the camera (●) for the experiments with an inert solvent (Table 3, entry 4).

are only appointed local temperatures (fiber-optics thermometer) or average temperatures (thermovision camera) that in the latter case correspond only to the temperature of surface, which is lower than the bulk temperature.

## 3. Conclusion

In conclusion, a proper temperature measurement in case of heterogeneous reaction mixture is very difficult. In order to maintain a good temperature homogeneity and make some comparison with the experiments under conventional conditions, an effective stirring has to be provided, perhaps, together with a small amount of an inert solvent. There is a general agreement that the application of fiber-optics thermometers is the reliable way to determine temperature under microwave conditions. Applying the thermovision camera, we found that for the reactions in heterogeneous systems under microwave irradiation, the temperature measurement with a fiber-optics thermometer can lead to serious errors like pyrometry; in particular for those experiments that are planned without any attention being paid to temperature homogeneity of the reaction mixture. In the latter case, a high temperature gradient within the reaction mixture generated by the microwaves leads to a higher conversion of reactants or/and reaction rates, which in turn might be a reasonable explanation to the so-called non-thermal microwave effects, i.e., an increase of reaction rates that is inadequate to the temperature of reaction medium. 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, temperature profiles (gradients), and, in particular, proper design of our experiments.

## 4. Experimental

All chemicals were purchased from Aldrich and used as received. The reactions were carried out in a single-mode microwave reactor with a continuous power regulation (SynthWave 402, Prolabo). The inlet at the top of the reactor allowed the application of the thermovision camera (Vigo V-20E2) and the introduction of the fiber-optics thermometer (ReFlex, Nortech), which was used to control the temperature during microwave experiments. GC/MS spectra were determined on GC/MS 5890 SERIES II HEWLETT–PACKARD gas chromatograph equipped with Ultra 2 (25 m×0.25 mm×0.25 μm) column with HEWLETT–PACKARD 5971 Series Mass Detector.

In a typical experiment, the reactions were carried out by simply mixing $K_2CO_3$ (2.70 g, 20 mmol), salicylaldehyde (0.61 g, 5 mmol), chloroacetic acid ethyl ester (1.22 g, 10 mmol), and a catalyst (TBAB 0.16 g, 0.50 mmol). Then the mixtures were irradiated for 3 min in an open quartz vessel (4 cm of diameter) in the microwave reactor or heated for 5 min in a thermostated oil bath (2 min were added in comparison to microwave experiments because of a thermal inertia of the vessel). Finally, the reaction mixtures were extracted with 20 ml of acetone to estimate overall yields by means of GC/MS.

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