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Microwave Effects

Microwave Chemistry in Silicon Carbide Reaction Vials: Separating Thermal from Nonthermal Effects**

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The use of microwave energy to enhance chemical reactions is growing at a rapid rate; new and innovative applications in organic and peptide synthesis, polymer chemistry, material sciences, nanotechnology, and biochemical processes are being reported continuously.[1] In many instances, microwave irradiation has been shown to dramatically reduce processing times, increase product yields, and enhance product purities or material properties over that reported for conventionally processed experiments.[1] Regardless of the relatively large body of published work in this field, there is still considerable controversy on the exact reasons why microwave irradiation is able to enhance chemical processes. In particular, there is an ongoing debate in the scientific community whether the observed enhancements are the result of purely thermal/kinetic effects as a consequence of the rapid heating and high bulk reaction temperatures that can be attained using microwave dielectric heating,[2] or whether they are related to selective interactions of the electromagnetic field with specific substrate molecules, reagents, or catalysts not connected to a macroscopic bulk temperature effect (so-called "specific" or "nonthermal" microwave effects).[3,4] Indeed, there is experimental evidence that certain chemical transformations, when carried out at the same measured reaction temperature using either microwave or conventional heating, lead to different results in terms of product distribution (selectivity) and/or yield.[3–5]

Herein we describe technology that makes it possible to rapidly evaluate whether an observed enhancement seen in a microwave-assisted chemical transformation is the result of a purely thermal phenomenon, or whether specific/nonthermal microwave effects are involved. Key to this method is the use of a reaction vessel made out of silicon carbide (SiC), in combination with a single-mode microwave reactor that allows simultaneous temperature monitoring by external infrared (IR) and internal fiber-optic probes (FO).[6] Silicon carbide is a strongly microwave-absorbing chemically inert ceramic material that can be utilized at extremely high temperatures owing to its high melting point (≈2700 °C) and very low thermal expansion coefficient.[7] Microwave irradiation induces a flow of electrons in the semiconducting SiC that heats the reaction vessel very efficiently through resistance (ohmic) heating mechanisms.[7] We have speculated that because of the high microwave absorbtivity of SiC, any material (i.e. a reaction mixture) contained within the vial will be effectively shielded from the electromagnetic field. This hypothesis was confirmed by heating experiments using solvents of vastly different microwave absorbtivity (loss tangent, $\tan\delta$)[2,3] at constant microwave power in which the heating profiles attained in a standard Pyrex vial were compared with the profiles in the SiC vessel. For this purpose a custom-made 10 mL reaction vial made out of sintered SiC of the exact same geometry as a standard microwave-transparent Pyrex microwave process vial was utilized (see Figure S1 in the Supporting Information). While the heating profiles obtained with the Pyrex vials followed the expected trend and were correlated to the $\tan\delta$ value of the solvent (Figure 1 a), the heating of solvents in the SiC vessel was apparently not related to their microwave absorbtivity, but rather dependent on other parameters such as specific heat capacity, viscosity, and heat-transfer coefficients (Figure 1 b).

The fact that in the SiC vial nearly microwave-transparent hexane ($\tan\delta = 0.02$) is heated at the same rate as the strongly absorbing EtOH ($\tan\delta = 0.941$) (Figure 1 b) clearly indicates that the microwave field intensity inside the SiC vial must be extremely low, and that heating occurs in essence by means of conventional heat-transfer mechanisms and not by dielectric heating effects.[2] This was further corroborated by immersing a Hg electrodeless discharge lamp (EDL, see Figure S2 in the Supporting Information)[9] into the SiC vial. Even when a 300 W magnetron output power was applied it was not possible to induce a gas discharge. In contrast, in a standard Pyrex vial 1–5 W of microwave power was sufficient to trigger gas discharge causing the emission of UV/Vis irradiation in these EDLs (see Figure S2 in the Supporting Information).[9]

A direct comparison of the heating profiles obtained in Pyrex and SiC vials for each of the four solvents discussed above (Figure 1) demonstrates that—with the exception of the strongly microwave-absorbing ionic liquid [bmim]PF_6—the solvents are generally heated at the same rate if not faster in the SiC vial as in the Pyrex vial, in particular in the high-temperature range (see Figure S3 in the Supporting Information). Similar to a standard microwave heating experiment, the use of higher power levels in the SiC vial leads to a more rapid heating of the solvent/reaction mixture (see Figure S4 in the Supporting Information). Importantly, heating experi-

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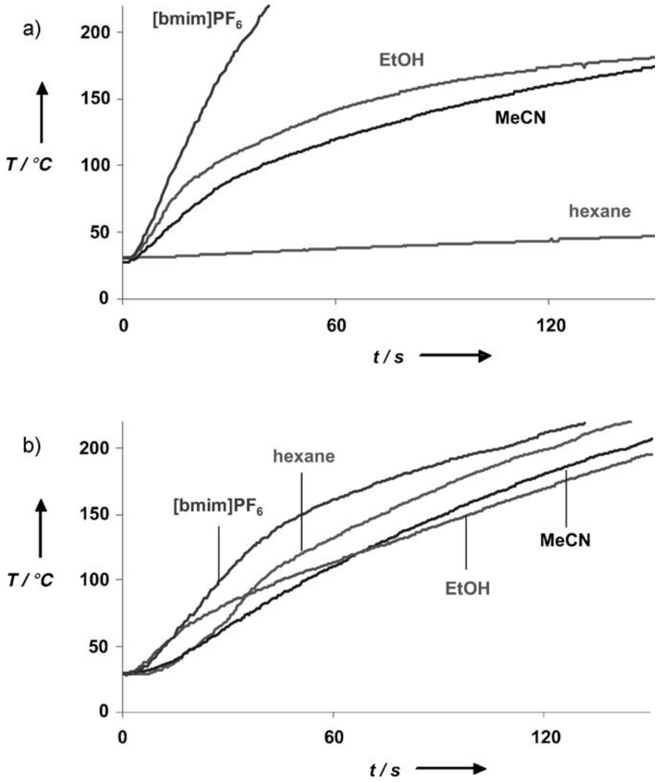
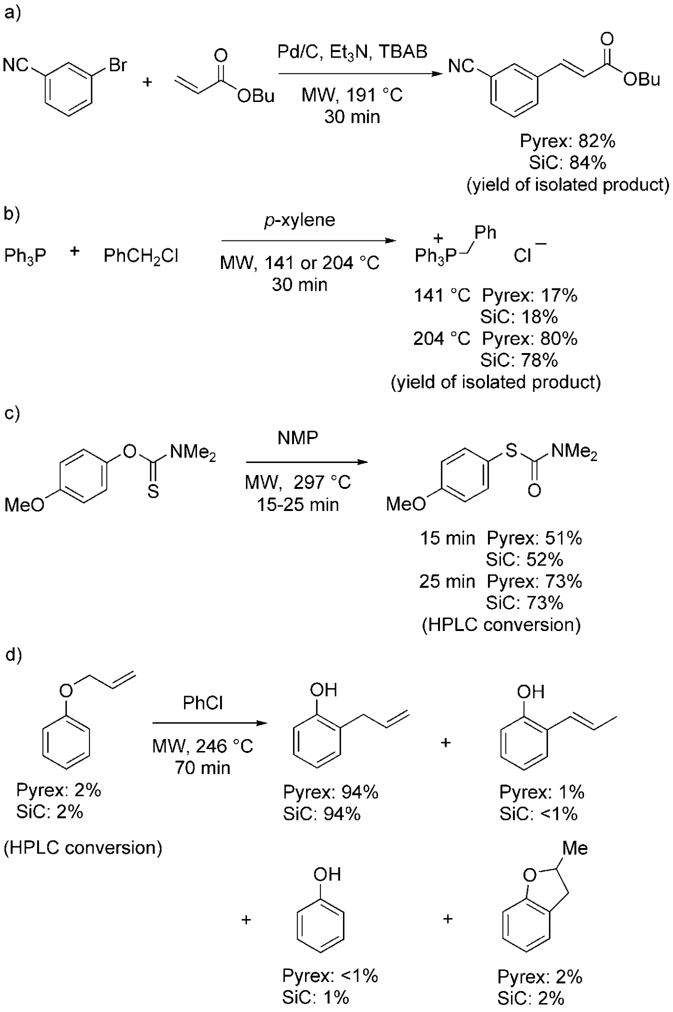


Figure 1. Heating rates for 3 mL samples of hexane ($\tan\delta = 0.02$),[3] MeCN ($\tan\delta = 0.062$),[3] EtOH ($\tan\delta = 0.941$),[3] and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF$_6$, $\tan\delta > 1$)[8] at 130 W constant magnetron power in a 10 mL Pyrex vial (a), and in a custom-made SiC vial (b). Single-mode microwave irradiation, magnetic stirring, internal fiber-optic temperature measurement.[6]

ments with SiC vials in single-mode microwave reactors can not only be performed in power control mode (Figure 1), but also in temperature control mode using either an internal fiber-optic sensor (FO), or an external infrared sensor (IR) to control the magnetron output power (see Figure S5 in the Supporting Information).

As a result of the high thermal conductivity of SiC (≈ 100 times higher than for Pyrex glass; see Table S1 in the Supporting Information)[7] the heat flow through the 1.8 mm wall of the SiC reaction vessel is exceptionally fast. In addition, owing to the extremely high thermal effusivity of SiC (a measure for the ability to exchange thermal energy with its surroundings)[10] the contents inside the SiC reaction vial are also heated in a very efficient manner (Figure 1 b). This unique combination of unusually high microwave absorbtivity, thermal conductivity, and effusivity of SiC makes this material ideal for use in microwave reactors. In essence, the technology described above allows us to use a standard single-mode microwave reactor platform to perform a non-contact-heating autoclave experiment under very carefully controlled and monitored conditions (heating and cooling ramp, final set temperature, pressure, stirring speed; see Figure S5 in the Supporting Information). Importantly, this experiment, although performed in a microwave reactor, does not involve electromagnetic field effects on the chemistry since the SiC vial effectively prevents the penetration of microwave irradiation to the reaction mixture.

The experimental setup described herein is well suited to investigate the significance of specific and nonthermal microwave effects; switching the vial from microwave-transparent Pyrex to a strongly microwave-absorbing SiC will prohibit any electromagnetic field effects from reaching the reaction mixture. At the same time the method retains sealed-vessel capabilities, enables rapid heating, and exhibits the excellent process-control features inherent to modern microwave reactors. We have applied this concept to a variety of previously published microwave-assisted transformations, where enhancements over the results obtained under standard reflux conditions (heated oil bath) have been observed (Scheme 1 and Scheme S1 in the Supporting Information). The chosen reactions involved both strongly and weakly microwave-absorbing solvents in a temperature range of 100–300 °C with reaction times of 1–70 min. Experiments were



Scheme 1. Conversions/yields obtained for sealed-vessel microwave experiments performed in Pyrex or silicon carbide reaction vials. Single-mode microwave irradiation, magnetic stirring, internal fiber-optic temperature measurement.[6] For heating and power profiles, see Figure S6 in the Supporting Information. TBAB = tetrabutylammonium bromide, NMP = *N*-methylpyrrolidone.

carried out on a 2–5 mL scale in both low- and high-boiling solvents, and included reactions that were either fully homogeneous or involved heterogeneous starting materials, reagents, or catalysts. Gratifyingly, for all examples it was possible to achieve similar internal FO temperature profiles in both Pyrex and SiC vials (see Figure S6 for selected heating curves); other process parameters such as pressure and stirring speed were also identical.

For the eighteen examples presented herein, virtually identical results in terms of conversion, purity profile, and/or product yields were obtained for experiments that involve genuine microwave chemistry in Pyrex vials and those with "microwave heating" in SiC vials (Scheme 1 and Scheme S1 in the Supporting Information). This confirms that for these cases only bulk temperature effects are responsible for the observed enhancements and that the electromagnetic field has no direct influence on the reaction pathway (specific or nonthermal microwave effects).[3,4] The results obtained for selected examples involving Mizoroki–Heck couplings,[11] the alkylation of triphenylphosphine with benzyl chloride,[5b] and Newman–Kwart[12,13] and Claisen rearrangements[7,13,14] are highlighted in Scheme 1. Additional case studies are presented in Scheme S1 in the Supporting Information.

The high thermal effusivity of SiC aids not only in the rapid heat transfer from the outside to the inside of the SiC reaction vial, but also in the reverse direction from the inside to the outside. This characteristic becomes important in the case of an exothermic reaction where the released heat often leads to a thermal overshoot or runaway in a conventional oil-bath or microwave experiment. A case in point is the formation of imidazolium-based ionic liquids by alkylation of 1-methylimidazole with an alkyl halide (Figure 2). Under microwave conditions, these transformations are notoriously difficult to control since not only is the N-alkylation exothermic, but in addition the microwave absorbtivity during the process changes significantly from moderate (starting materials) to high (ionic liquid).[8,15] In order to investigate the performance of the SiC reaction vial in the preparation of [bmim]Br we first evaluated the exothermicity of this process by performing the solvent-free preparation of [bmim]Br using a Pyrex vial in an oil bath preheated to 100 °C with simultaneous internal temperature measurement. At around 90 °C the reaction becomes strongly exothermic, leading to an internal temperature of nearly 160 °C within a few seconds (see Figure S7 in the Supporting Information). When the same reaction was performed in the microwave reactor using a set temperature of 100 °C and the standard Pyrex vial, a similar overshoot of ≈40 °C was observed (Figure 2). In striking contrast, using the SiC vessel, the ≈10 times higher thermal effusivity (Table S1 in the Supporting Information) prevents the occurrence of an overshoot since the heat generated during the formation of the ionic liquid is efficiently exchanged with the comparatively cool air in the microwave cavity via the SiC ceramic.

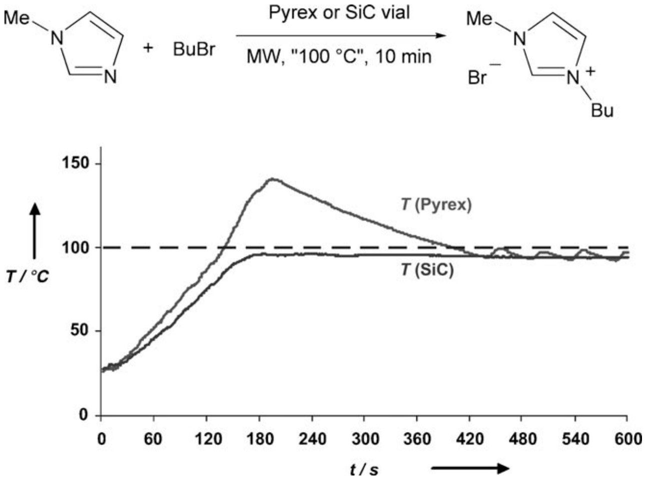


Figure 2. Internal fiber-optic temperature profiles for the solvent-free synthesis of the ionic liquid [bmim]Br using Pyrex and SiC reaction vials. Experiments were performed using an IR-controlled set temperature of 100 °C on a 10.6 mmol scale (1.02 equiv of BuBr).[6]

In conclusion, we have demonstrated that by using reaction vials made out of silicon carbide (SiC) ceramic in microwave reactors one can mimic a conventionally heated autoclave experiment, while retaining the rapid heating (flash heating) and excellent process control features inherent to microwave chemistry. The combination of high microwave absorbtivity, thermal conductivity, and thermal effusivity of SiC allows very rapid heat exchange with its surroundings which is not only important for the rapid heating of the reaction mixtures, but can also prevent exotherms attributed to the noncontact-heating nature of this technology. Other benefits of SiC vials include their high chemical resistance which allows the use of corrosive reagents not suitable for processing in standard glass vials,[16] and the high temperatures that can be attained rapidly by exposure to microwave irradiation (Figure S1 in the Supporting Information). Most importantly, the method described herein makes it possible to rapidly separate thermal from specific/nonthermal effects, since by employing the SiC vial any effects of the electromagnetic field on the reaction mixture can be eliminated. Future work using this technology will be aimed at studying the specific benefits of microwave irradiation on a set of more complex transformations ranging from organic and polymer synthesis to nanomaterials research.

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[1] For a recent review with more than 900 references and a tabular survey of ca. 200 microwave chemistry review articles, books, and book chapters, see: C. O. Kappe, D. Dallinger, *Mol. Diversity* **2009**, *13*, 71.

[2] For reviews on dielectric heating, see: a) C. Gabriel, S. Gabriel, E. H. Grant, B. S. Halstead, D. M. P. Mingos, *Chem. Soc. Rev.* **1998**, *27*, 213; b) D. M. P. Mingos, D. R. Baghurst, *Chem. Soc. Rev.* **1991**, *20*, 1.

[3] For a definition and examples for thermal, specific, and nonthermal microwave effects, see: a) C. O. Kappe, *Angew. Chem.* **2004**, *116*, 6408; *Angew. Chem. Int. Ed.* **2004**, *43*, 6250; b) C. O. Kappe, D. Dallinger, S. S. Murphree, *Practical Microwave Syn-*

thesis for Organic Chemists—Strategies, Instruments, and Protocols, Wiley-VCH, Weinheim, **2009**, pp. 20–44.

[4] For leading reviews, see: a) L. Perreux, A. Loupy, *Tetrahedron* **2001**, *57*, 9199; b) L. Perreux, A. Loupy in *Microwaves in Organic Synthesis*, 2nd ed. (Ed.: A. Loupy), Wiley-VCH, Weinheim, **2006**, chap. 4, pp. 134–218; c) A. De La Hoz, A. Diaz-Ortiz, A. Moreno, *Chem. Soc. Rev.* **2005**, *34*, 164.

[5] It should be emphasized, however, that it is rather difficult to perform appropriate control experiments to compare microwave- and conventionally heated processes in an oil bath or autoclave, since these must be conducted at the exact same temperature (including heating and cooling profiles); other processing details such as vessel geometry, stirring speed, and the method of temperature monitoring should ideally also be identical. For a discussion, see: a) M. Hosseini, N. Stiasni, V. Barbieri, C. O. Kappe, *J. Org. Chem.* **2007**, *72*, 1417; b) M. A. Herrero, J. M. Kremsner, C. O. Kappe, *J. Org. Chem.* **2008**, *73*, 36.

[6] Experiments were performed in a commercial 2.45 GHz single-mode microwave reactor from Anton Paar GmbH (Monowave 300). For further details, see the Supporting Information and http://www.anton-paar.com/monowave300.

[7] J. M. Kremsner, C. O. Kappe, *J. Org. Chem.* **2006**, *71*, 4651, and references therein.

[8] S. Horikoshi, T. Hamamura, M. Kajitani, M. Yoshizawa-Fujita, N. Serpone, *Org. Process Res. Dev.* **2008**, *12*, 1089.

[9] P. Klán, V Církva in *Microwaves in Organic Synthesis*, 2nd ed. (Ed.: A. Loupy), Wiley-VCH, Weinheim, **2006**, chap. 19, pp. 860–897.

[10] The thermal effusivity e of a material is defined as the square root of the product of its thermal conductivity and volumetric heat capacity [$e = (k\rho c_p)^{0.5}$]. The thermal effusivity of the SiC used in these studies (Ekasic F SSiC, ESK Ceramics) is ≈ 10 times higher than that of standard Pyrex glass. See Table S1 in the Supporting Information.

[11] T. N. Glasnov, S. Findenig, C. O. Kappe, *Chem. Eur. J.* **2009**, *15*, 1001.

[12] J. D. Moseley, P. Lenden, *Tetrahedron* **2007**, *63*, 4120.

[13] T. Razzaq, T. N. Glasnov, C. O. Kappe, *Eur. J. Org. Chem.* **2009**, 1321.

[14] T. Razzaq, J. M. Kremsner, C. O. Kappe, *J. Org. Chem.* **2008**, *73*, 6321.

[15] a) M. Deetlefs, K. R. Seddon, *Green Chem.* **2003**, *5*, 181; b) T. Erdmenger, R. M. Paulus, R. Hoogenboom, U. S. Schubert, *Aust. J. Chem.* **2008**, *61*, 197.

[16] J. M. Kremsner, M. Rack, C. Pilger, C. O. Kappe, *Tetrahedron Lett.* **2009**, *50*, 3665.