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

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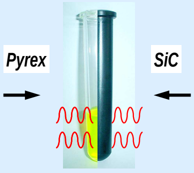
❶ The Concept of Microwave Chemistry in Silicon Carbide Reaction Vessels

Microwave Chemistry without Microwaves !



Microwave Heating ! → ← *Conventional Heating !*

High speed organic synthesis in dedicated microwave reactors is on the leap to become a standard tool for most organic chemists working in both academic and industrial laboratories.
However, there is an ongoing debate in the scientific community on whether the observed dramatic accelerations of reaction rate are mainly a consequence of the high bulk temperatures attained in microwave chemistry, or whether there is a significant contribution of "nonthermal" effects (e.g. a decrease in transition state energies by direct molecule-field interactions not related to a macroscopic temperature-effect), or "specific " microwave effects (e.g. selective heating of catalyst particles).

Using ceramic reaction vials made out of strongly microwave-absorbing silicon carbide (SiC) in a microwave reactor simulates experiments conducted in an autoclave with conductive heating because of the efficient shielding of the electromagnetic field by the SiC vial.

By comparison of the yields and product distributions in chemical transformations conducted in both Pyrex and SiC vessels under otherwise completely identical conditions, it can be determined in a simple experiment, whether an observed enhancement in the chemical reaction is related to a bulk temperature effect or whether specific/non-thermal effects are involved.

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❷ Sintered Silicon Carbide (SSiC): A Vessel Material with Unique Material Properties

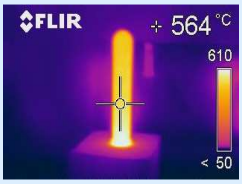
Sintered 10 ml Vessels

- mp > 2700 °C; density 3.10 g/cm³
- very low thermal expansion coefficient
- high thermal shock resistance
- no phase transitions known

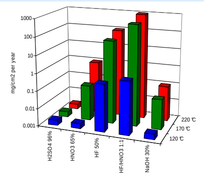
- ***strong microwave absorber***
- ***100 fold thermal conductivity of glass***
- ***virtually universal corrosion resistance***

10 ml Pyrex / SiC vessels

SiC vial (1400 W, 2-3 min)



*Corrosion Resistance**



*Meschke, F.; Riebler, G.; Hessel, V.; Schürer, J; and Baier, T. *Chem. Eng. Technol.* **2005,** 28, 465.

❸ Proof of Concept 1: Microwave Shielding

A: Investigation of Heating Profiles

To investigate the electromagnetic field inside the SiC vessels, the heating rates of four solvents ranging from microwave transparent to strongly microwave absorbing were investigated.

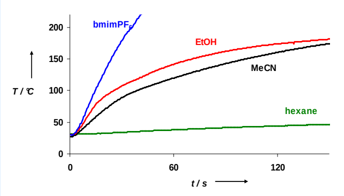
Strongly Absorbing

tanδ (bmimPF_6) > 1; tanδ (EtOH) = 0.941

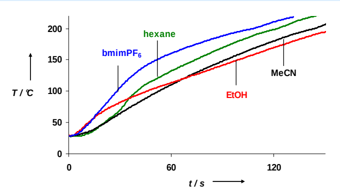
Weakly Absorbing

tanδ (MeCN) = 0.062; tanδ (hexane) = 0.02

a) Borosilicate Glass ("Pyrex")



b) Sintered Silicon Carbide (SSiC)

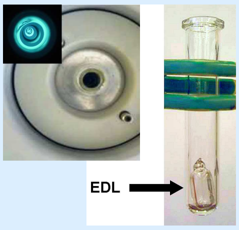


a) In Pyrex the four solvents heat faster or slower, according to their individual tanδ-values.

b) *In SiC the heating of the four solvents appears to be independent of individual tanδ-values*.

This clearly indicates that the electromagnetic field is to large extent absorbed by the ceramic vessel walls and converted to heat, which is then dissipated into the liquid by conventional heat transfer mechanisms, such as convection currents.

B: Electrodeless Discharge Lamps (EDLs)



To further corroborate the results obtained by using solvents with vastly different microwave absorptivities, electrodeless discharge lamps (EDLs) were placed inside both SiC and Pyrex vials and the vials irradiated at different magnetron powers.

EDLs contain a small amount of Hg under noble-gas atmosphere and interact very efficiently with the electromagnetic field.
When placed in a Pyrex reaction vial in a single-mode microwave reactor, ignition of the lamps was observed between 1-5 W nominal magnetron power.

A completely different result was obtained for the same experiment in silicon carbide vials, where *no ignition of the lamps could be triggered*, even at the maximum magnetron power of 300 W.

❺ Proof of Concept 2: Temperature Controlled Flash Heating in a Commercial Single-Mode Reactor

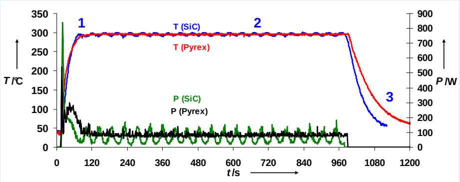
Process Control Features - SiC vs. Pyrex Vessels

Monowave 300

Anton-Paar GmbH (Graz, Austria)

- 850 W single mode reactor
- very high field densities
- operation up to 300°C/30 bar
- internal fiber-optic thermometer

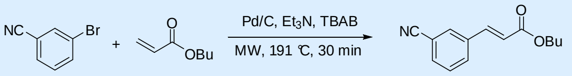
Temperature-Profiles in a Newman - Kwart Reaction



1 microwave flash heating in 1.5 min to 300 °C as rapid as with Pyrex
2 good control of hold temperature with default control algorithm
3 improved cooling performance using SiC (2 vs. 4 min cooling)

❻ Chemistry Examples in Pyrex vs. SiC

Mizoroki-Heck Cross-Coupling

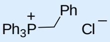


SiC	Pyrex
84%	82%

(isolated yield)

Alkylation of Triphenylphosphine

Ph_3P + $PhCH_2Cl$ $\xrightarrow[\text{MW, 141 or 204 ℃, 30 min}]{p\text{-xylene}}$

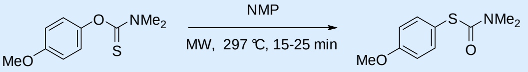


$Ph_3P^+CH_2Ph\ Cl^-$

	SiC %	Pyrex %
141 °C	18	17
204 °C	78	80

(isolated yield)

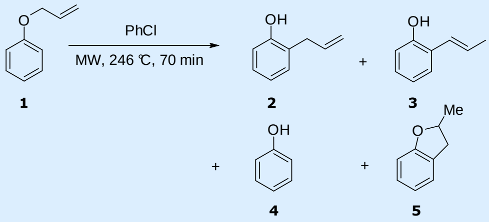
Newman-Kwart Rearrangement



	SiC %	Pyrex %
15 min	52	51
25 min	73	73

(HPLC 254 nm)

Claisen Rearrangement



	SiC %	Pyrex %
1	2	2
2	94	94
3	<1	1
4	1	<1
5	2	2

(HPLC 215 nm)

A total of 18 chemistry examples, where enhancements in yield, purity, or reaction-rate over standard-reflux conditions were reported, were performed in both SiC and Pyrex vessels.

Under precise temperature control (internal fiber-optic probe) and identical heating profiles for both Pyrex and SiC, experiments performed under both dielectric heating (Pyrex) and wall heating (SiC) gave identical results.

❼ Conclusions and Outlook

- Strongly microwave-absorbing ceramic SiC-vessels in a microwave reactor can be used to mimic conventionally heated autoclave experiments, while retaining the excellent process control features inherent to modern microwave reactors.

  It should be noted at this point, that it is by conventional means (e.g. oil-bath heating, heating mantles etc.) very difficult to reproduce the sharp heating-profiles obtained in microwave heating and that because of the exponential relationship between reaction rate and temperature, small deviations in temperature profiles can have a large impact on yield and product distribution.

  Thus, the combination of SiC vessels in conjunction with a high field-density microwave reactor (single-mode reactors), seems to be the perfect tool for the investigation of microwave effects.

- Preliminary results of experiments performed in both Pyrex and SiC under otherwise completely identical conditions identified only the high bulk-temperatures attained in microwave heating as main accelerating effect (Arrhenius-law).

- Future work will be aimed at studying more complex transformations ranging from organic and polymer synthesis to nanomaterials research.

Hot Paper in

Obermayer, D.; Gutmann, B., and Kappe, C. O.
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