



Determination on temperature gradient of different polar reactants in reaction mixture under microwave irradiation with molecular probe



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ABSTRACT

Temperature accurate measurement is one of key issues in illustration of the rate increase in the microwave-promoted organic reactions because reaction rates are closely related with reaction temperature. The use of molecular probe is reported as a tool to identify the microwave selective heating effects in homogenous reaction mixture of intramolecular aromatic Claisen rearrangement. Our results show direct evidence for localized superheating of polar reactants in nonpolar solvent. While in the polar solvent, the microwave selective heating effects of polar reactants will be decreased.

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1. Introduction

Since the first published report in 1986,¹ microwave-assisted organic synthesis has been widely developed. Virtually all types of thermally driven chemical reactions have been studied under microwave irradiation.² Under microwave irradiation conditions, some organic reactions can be accelerated obviously. In some cases, this powerful technique can produce higher yields, different selectivity, and lower side products.³ Such useful performances of microwave irradiation (MWI) have sparked considerable speculations and discussions into the essence of the microwave heating. Much of the debate has focused on the question whether the acceleration can be rationalized by purely thermal effects or some specific microwave effects.⁴

Nonthermal microwave effects^{4a,c} were speculated previously as results from the directly coupling interaction between microwave electric field and polar molecules (reactants, intermediates, and even transition states) in the reaction mixtures, which did not generate a macroscopic change in reaction temperature. It was argued that microwave electric field affected the orientation of polar molecules or intermediates and hence changed the pre-exponential factors A or the activation energies in the Arrhenius

equation for certain types of reactions.^{4a,d} However, some of the further studies on the hypothesized nonthermal effects were proven incorrect later. Subsequent careful reinvestigations revealed that the reaction results were quite close to those of the conventional reactions run at the same temperature. The so-called 'microwave effects' were mainly due to the flawed temperature measurement of the reaction mixture or subtle differences of reaction conditions.^{4e,5}

The vast majority of microwave accelerated reactions can be explained as the thermal effects arising from the extremely fast heating rate, which cannot be reproduced by classical heating. By using an external heat source, heat first passes through the walls of the vessel and then reaches the reaction mixture. It results in the temperature of reaction mixture being lower than that of the vessel until sufficient time to achieve thermal equilibrium. Microwave irradiation, on the other hand, directly couples with the molecules inside the reaction mixture, leading to a rapid rise in temperature.⁶ Microwave irradiation does not change the activation energy, but provides the momentum to overcome the energy barrier of reactions more quickly. In addition, the 'inverted heat transfer' effect⁷ (from the reaction mixture towards the exterior) can arouse the overheating of liquids above the normal boiling point,⁸ since boiling nuclei are formed at the surface of the liquid. This overheating effect could explain the acceleration of reactions.

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While some specific reaction results under microwave irradiation could not be rationalized simply by rapid heating or flawed temperature measurement. For example, Yamada and co-workers reported a copper triflate-catalyzed asymmetric Claisen rearrangement,⁹ in which the reaction was accelerated under the microwave irradiation without a corresponding decrease in enantioselectivity. The linear relationship between $\ln[ee]$ and $1/T$ was revealed that the enantioselectivity decreased as the internal reaction temperature increased.

MW energy directly heats specific molecules in the reaction mixture through the loss processes. For a specific molecule, the ability to convert microwave energy into heat is determined by the loss tangent ($\tan \delta$).⁶ Compounds with high loss tangent tend to absorb the MW energy whereas less polar substances are poor absorbers. In this way, absorption of the radiation and heating may perform selectively.

Huang and Richert proposed a microwave selective heating model that the flow of microwave irradiation can potentially trigger the selective heating of a dipolar molecule in a non-absorbing solvent.¹⁰ The microwave absorbing molecules ('domains') assimilate microwave energy and accumulate the heat, resulting in an instantaneous localized superheating ('hot spots'). The amount of accumulated heat can potentially give rise to microwave specific rate enhancement.

Schmink and Leadbeater used *in situ* Raman spectroscopy as a tool for probing the selective heating effects of microwave irradiation.¹¹ Raman monitoring can detect reaction mixture on a microscopic level. While the microwave energy may interact with the polar molecules more so than with nonpolar ones, the results indicate that more polar molecules are not at a higher temperature. They conclude that the reason is that the conversion of electromagnetic energy into kinetic energy is slower than conversion of kinetic energy into thermal energy. That is, the selective heating of microwave irradiation could not cause the microscopic 'hot spots'.

The experimental evidence of MW selective heating that is in accord with the model of Huang and Richert was reported by Dudley's group.¹² They observed detectable heat accumulation and microwave specific rate enhancement for the aromatic Claisen rearrangement of allyl 4-nitrophenyl ether in benzene (a nonpolar solvent). The effective temperatures calculated from the measured reaction rate based on Arrhenius plots were higher than the temperature measured by the calibrated internal fiber probe, demonstrating the excess heat is accumulated in the 'domain' and resulting in a reaction accelerating. This unique MW selective heating mechanism cannot be duplicated by convective heating process.

Generally, in order to evaluate or to attest the existence of MW effects, the temperature of the reaction mixture must be accurately measured. Unfortunately, currently common temperature monitoring devices, such as external infrared monitors and internal fiber monitors, are not the best choices to measure the internal temperature of reactions veritably and accurately.^{4e,13} External infrared temperature monitors record the temperature on the outer surface of the reaction vessel and do not precisely reflect the temperature of the reaction mixture. Internal fiber-optic monitors are more accurate but only measure the temperature at several single positions of the reaction mixture. Importantly, in selective heating mechanism, the 'domains' can directly couple with microwave energy and thus create microscopic hot spots at the molecular level. The temperature gradient between 'domains' and surroundings, if exists, cannot be measured by commercially available temperature monitoring devices.

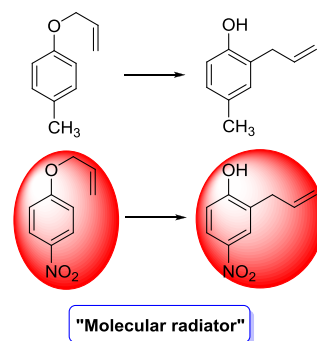
Molecular probes have advantage in the measurement of internal temperature of reaction mixture on molecular level compared with the physical temperature monitoring devices. Our group used diastereoselectivity in the Staudinger reaction as

a useful probe for investigation of nonthermal microwave effects.^{14,15} The results indicate that no obvious effect of microwave irradiation on the diastereoselectivity was observed in the Staudinger reactions. The increase of polarity of intermediates did not accelerate the reaction or alter the diastereoselectivity.

In this study, our group uses reactant molecules as a temperature probe in an effort to identify the microwave selective heating effects in homogenous reaction mixture. In this way, temperature gradient can be directly observed.

2. Results and discussion

For a specific material or solvent, the ability to convert microwave energy into heat at a given frequency and temperature is determined by the so-called loss tangent ($\tan \delta$). The value of loss tangent is expressed as $\tan \delta = \epsilon''/\epsilon'$, where ϵ'' is the dielectric loss, indicative of the efficiency with which the electromagnetic radiation is converted to heat, and ϵ' is the dielectric constant describing the polarizability of molecules in the electric field. In general, materials with large permanent dipole moment could strongly absorb microwave energy and, consequently, for efficient heating.^{5,7} In this study, we prospect to use a two-substrate-based aromatic Claisen rearrangement of allyl 4-nitrophenyl ether (ANE) and allyl 4-methylphenyl ether (AME) as a tool for probing the selective heating effect of microwave irradiation on molecular level (Scheme 1). Aromatic Claisen rearrangements are suitable as model reactions because they are typical intramolecular reaction followed simple first-order kinetics. The effective temperature is easy to be obtained from the measured rate constants and Arrhenius Equation. With a significantly large dipole moment, ANE could effectively convert MW energy into heat, and the accumulated heat will, in our hypothesis, potentially create a high thermal energy 'domain', whereas the weak-polar AME could slightly absorb the MW energy and only be heated by the surroundings through the convective heating in polar solvent. Therefore, AME is considered likely to be suitable as a temperature probe for the bulk solution. This protocol does not require calibrated temperature monitoring devices and the strict control of microwave reactor. It can simulate the reaction conditions applied widely in microwave-assisted organic reactions.



Scheme 1. Two-substrate-based aromatic Claisen rearrangement of allyl 4-nitrophenyl ether (ANE) and allyl 4-methylphenyl ether (AME).

Solvents play a very important role in microwave-assisted organic reactions. The more polar a solvent is, the greater its ability to couple with the microwave energy and the faster the temperature of the reaction mixture increases. Clearly, the solvent effect is of great importance with regard to the possibility of the microwave selective heating. We conducted the same Claisen rearrangements under microwave irradiation both in a polar solvent (*N*-methylpyrrolidone, NMP, a favorable microwave absorbance solvent with loss factor $\tan \delta$ 0.275) and in a nonpolar one (*n*-tetradecane). All of

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