

## §7. Theoretical Study of Nonthermal Microwave Effects on Intramolecular Reactions

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There have been a growing number of articles that report dramatic improvements in product yield of chemical reactions and/or reduction of reaction time by microwave irradiation compared to that under classical heating conditions. It is however still unclear whether the microwave effects on enhanced reactions are in fact thermal or nonthermal. The thermal effects of microwaves are attributed to the rise in solvent temperature due to dielectric loss. The nonthermal effects collectively mean those that cannot be included in the thermal effects, e.g., the direct interaction of the microwave field with the electric dipoles of solute molecules. Recently, separation of thermal and nonthermal effects has been attempted by the experiments using a reaction vessel made out of silicon carbide (SiC).<sup>1</sup> The material inside the vessel is effectively shielded from an applied radiation field owing to the high microwave absorptivity of SiC but quickly heated by the ohmic resistance to the conduction current flowing in the semi-conducting SiC under microwave irradiation. The results of 21 inter- and intramolecular reactions performed in SiC and standard microwave-transparent Pyrex vials show that the product yields in both cases were almost identical at the same reaction temperature and time.<sup>1</sup> This indicates that a microwave field has no direct (nonthermal) effect on the selected chemical reactions.

We examined the existence of nonthermal microwave effects on intramolecular reactions by evaluating thermal effects using the transition state theory, which provides the rate constants for elementary reactions at a given temperature.<sup>2</sup> The theoretical rate constant for the Newman-Kwart rearrangement (NKR) with a 4-methoxyphenyl group (Figure 1) is compared to the experimental data under microwave irradiation<sup>1</sup> in Table 1. The rate constant predicted by the transition state theory agrees well with the experimental one. This supports that the enhancement of NKRs is due to thermal heating effects alone. The intramolecular Diels-Alder reaction (IDAR) in Figure 2 driven by microwave irradiation has been reported to be about twenty times faster than that under toluene reflux.<sup>3</sup> However, the temperatures for these two processing conditions were different. The calculated values of the rate constant for the

IDAR in a reflux or microwave condition accounts for the increase in the reaction rate by microwave irradiation but are smaller than the respective values of the experimental one about 1 order of magnitude (Table 2). There remains room for the existence of nonthermal contribution to this reaction.

This approach based on the transition state theory should be combined with the results obtained by the experimental technique in which nonthermal effects can be separated from thermal ones by controlling microwave penetration through a reaction vessel.<sup>1</sup> The combination of the experimental and theoretical procedures is promising to reveal the role of microwaves in chemical reactions more in detail.

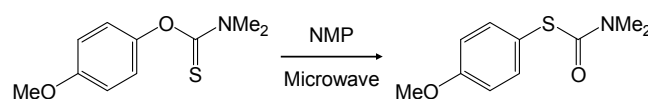


Figure 1: NKR with a 4-methoxyphenyl group.<sup>1</sup>

Table 1: Experimental and theoretical rate constants for the NKR in Figure 1.

Temp (°C)	Time (min.)	Yield (%)	Rate constant (s <sup>-1</sup> )	
			Experiment	Theory
297	15	52	8.2 × 10 <sup>-4</sup>	1.1 × 10 <sup>-3</sup>
	25	73	8.7 × 10 <sup>-4</sup>	

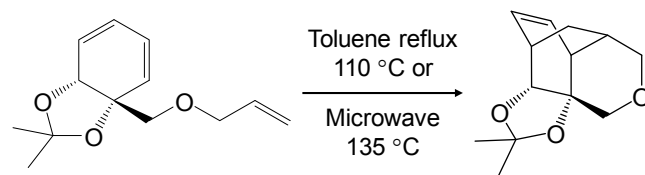


Figure 2: IDAR performed under reflux or microwave condition.<sup>3</sup>

Table 2: Experimental and theoretical rate constants for the IDAR in Figure 2.

Temp (°C)	Time	Yield (%)	Rate constant (s <sup>-1</sup> )	
			Experiment	Theory
110	3 days	93	1.0 × 10 <sup>-5</sup>	1.9 × 10 <sup>-6</sup>
135	200 min.	94	2.3 × 10 <sup>-4</sup>	1.7 × 10 <sup>-5</sup>

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2. M. Kanno *et al.*, Theoretical Verification of Nonthermal Microwave Effects on Intramolecular Reactions, *J. Phys. Chem. A* **116**, 2177–2183 (2012).
3. M. D. Mihovilovic *et al.*, Microwave-mediated intramolecular Diels–Alder cyclization of biodihydroxylated benzoic acid derivatives, *Tetrahedron Lett.* **45**, 7087–7090 (2004).