How Could and Do Microwaves Influence Chemistry at Interfaces?

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Many chemical reactions may be accelerated by order(s) of magnitude when exposed to microwaves. Reaction selectivities are often enhanced. Reasons for microwave reaction enhancements are speculative, often conflicting. We have demonstrated that microwaves can change the energies and/or the "effective temperature" of individual species at interfaces. Changes in the relative energies of reacting species or intermediates are shown by Monte Carlo simulation to lead to the observed enhancements in reaction rates or selectivities. Moreover, variations in microwave exposure in time or space can result in significant rate enhancement. Such variations may provide unique rate control.

1. Introduction

1.1. Microwave Chemistry. The recent American Chemical Society monograph on Green Chemistry[1] recommends that we "*Use methods that minimize the energy required for a reaction to take place. For example... catalysts or* **microwave radiation***...*".

Microwave energy is more efficient and selective in heating many processes. Materials differ by orders of magnitude in their ability to absorb microwave energy and/or to convert it to heat. The relevant material properties are the dielectric permittivity (ϵ') and loss (ϵ''), respectively (often expressed as a "complex permittivity"), and are both frequency- and temperature-dependent. Thus, systems containing two or more materials of significantly different permittivities can be heated in such a way to heat components selectively. If the portion of a system with the greatest ability to absorb microwaves (i.e., higher ϵ'') is the portion requiring the most heat, less overall energy is required for the process.

Many catalyst supports are essentially transparent to microwaves; examples are silica, alumina, zeolites, and many other oxides. The supported catalytic components are often metals, metallic compounds, acids, bases, and other reactive components. These are often orders of magnitude more susceptible to microwave absorption and heating. As a consequence, catalytic reactions in the presence of microwaves may be initiated at lower "system" temperatures than for conventional heating.[2] Because of this local heating, microwave heating can require considerably less energy than the conventional heating processes employing conductive and/or convective energy transfer, wherein the whole system, including the reaction vessel, must be raised to the desired reaction temperature.

Surface reaction selectivities are often enhanced by microwave heating as well, and sometimes different products are formed in the presence of microwaves. However, few studies discuss the effect of microwave energy on the sorption process.[3] Microwaves can influence the sorption process, as shown by Turner et al.[4] and Vallee and Conner.[5] While gaseous species are relatively transparent to microwaves, sorbed surface species can be very susceptible to microwave absorption. There is evidence that microwave energy can control the adsorption of one species over another in binary systems.[4]

Microwaves have been demonstrated to enhance many organic chemical reactions.[6,7] Microwave heating has also been shown to promote the syntheses of many solid materials. Many are heterogeneous reactions involving nucleation and growth upon the interfacial surface. These have been reviewed by Cundy[8] and more recently by Tompsett, Yngvesson, and Conner.[9]

1.2. Explanations for Microwave Enhancement. Several hypotheses have been advanced to explain the enhancement in reaction rates due to microwave exposure:

I. Microwave energy heats the reaction mixture more rapidly, increasing the net rate early in the heating process.[10]

II. Microwave energy leads to a more uniform heating of the reactor.[11]

III. Microwaves change the association between species within the reacting mixture.[12,13]

IV. Microwave heating superheats the reaction mixture.[14]

V. Hot spots are created within the reacting mixture (in contrast with II).[15,16]

VI. Microwave energy enhances the dissolution of reacting species.[13,17,18]

We have suggested[9] that specific reactions might be enhanced as a result of the absorption of microwave energy by reactants, intermediate-species, and/or products. This study focuses on this approach and whether microwave adsorption changes the temperatures or the energies of the intermediate states.

2. Relating Microwave Heating to Reaction Rate Enhancement

Many explanations for microwave enhancement have focused on the differences in the temperature profile created (I, II, IV, or V, above). Other kinetic analyses suggest that the influence of microwave exposure is to decrease the overall activation energy for a kinetic process. Each explanation is offered as the sole rationale for the documented rate enhancement due to microwave exposure. We discuss several questions that will place these hypotheses in perspective, wherein the subscript "μ" indicates under the influence of microwaves, viz:

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TABLE 1: Temperature Increases, ΔT_μ, Observed with Microwave Heating[a]

material/system	microwave system, temperature measurement	permittivity and loss (ϵ'/ϵ'')	temperature variations ΔT_μ (K)	enthalpy change ΔH (kJ mol^{-1})	type or effect	ref
MFI precursor gel	50 g liquid gel in Teflon vessel, CEM MDS 2000, 650 W max, FOP	60/25	45 K (greater than 80 °C) periphery		macroscopic overheating	19,33
LTA precursor gel	50 g liquid gel in Teflon vessel, CEM MDS 2000, 650 W, FOP	4/160	45 K (greater than 80 °C) periphery		macroscopic overheating	19,33
VFI precursor gel	50 g liquid gel in Teflon vessel, CEM MDS 2000, 650 W, FOP	20/15	40 K (greater than 80 °C) periphery		macroscopic overheating	19,33
organic solvents	waveguides, 75 W, 20 mLIR sensor, FOP		up to 40 K higher than boiling point, depends on MW power		superheating	21
n-pentane on silicalite	waveguide, 120 W, FOP	1.80/NA	2.67, pressure dependent	0.36	effective surface temperature	5,34
cyclohexane on Aerosil 200	waveguide, 120 W, FOP	2.02/0.05	7.86, pressure dependent	0.75	effective surface temperature	5,34
dichloromethane on Aerosil 200	waveguide, 120 W, FOP	9.08/0.39	16.58, pressure dependent	1.45	effective surface temperature	5,34
2-propanol on Aerosil 200	waveguide, 120 W, FOP	18.30/3.19	39.66, pressure dependent	6.82	effective surface temperature	5,34
dichloromethane on silicalite on	waveguide, 120 W, FOP	9.08/0.39	22.85, pressure dependent	3.70	effective surface temperature	5,34
isopropanol on silicalite	waveguide, 120 W, FOP	18.30/3.19	42.37, pressure dependent	5.15	effective surface temperature	5,34
imidization of a sulfone and ketone contg. polyamic acid	waveguide applicator, 85 W, FOP		54 K at 150 °C 50 K at 160 °C in vicinity of the dipole moment		microscopic temperature differences	31,34
silicon and diamond	waveguide, 300 W, Raman band shift, thermal probe simulation		100 K		macroscopic overheating	35
methanol and benzene on NaY & DAY zeolites			~200 K between benzene-C and methanol-O ; ~110 K between benzene and methanol center of mass: 1:1 per unit cell		microscopic	28

[a] A fiber-optic probe (FOP) was often employed.

A. What differences in temperature result from microwave exposure, ΔT_μ?

B. What changes in reaction activation energies have been estimated with microwaves, $E_{a\mu}$?

C. Is the net effect of microwaves due to a change in temperature or activation energy?

D. Are reactions at interfaces particularly susceptible to microwave enhancement?

2.1. Microwave-Induced Temperature Differences, ΔT_μ. Temperature variations in materials heated by microwaves have been reported for many systems; although, these have been cited to contribute to microwave reaction enhancement over a broad variation of length scales. On a macroscopic scale, superheating and hot spots have been noted; on a molecular scale, individual species or complexes are differentially heated; on an intermolecular scale, microwaves can be selectively absorbed by bonds or atoms.

On a macroscopic scale, superheating[19−26] and "hot spots"[15,16] have often been invoked to explain the reaction rate enhancement due to microwave exposure. "Superheating" is assumed to pertain to the total reaction system covering the whole reactor employed.[21,25−27] Hot spots are cited when it is believed that the system is not uniform but varies in position. The length scales of these "hot spot" temperature variations are comparable to the wavelength of the microwaves (~12.24 cm for radiation at 2.45 GHz in air).

Auerbach pioneered the analysis of differential heating at the other extreme, less than 1 nm, by atomic-scale simulation of competitive sorption in a zeolite.[28] His simulations replicate the experimental phenomena for competitive adsorption. They[28,29] conclude that energy is initially transferred to select molecular modes (translation, vibration, and/or rotation) as a result of microwave exposure. For example, Blanco et al.[28,29] simulated benzene and methanol adsorbed in NaY zeolite heated with microwaves. When benzene and methanol are adsorbed in the zeolite pore, the methanol heats to a much higher temperature compared to benzene because of its superior interaction with the field, giving a relative temperature difference of ~110 K.

On a molecular scale, West and Clark[30] proposed a theory for the mechanism of microwave heating involving the coupling of vibrational modes (overtones), which are of similar frequency to the microwave field. Others have suggested that molecularly associated intermediates (e.g., solvated species) are specifically heated by microwaves.[12,13,17,18]

Lewis et al.[31] also describe a mechanism based on temperature differences for the microwave-enhanced reaction of imidization of a sulfone and ketone group-containing polyamic acid. The apparent activation energy was reduced from 105 to 55 kJ/mol under the experimental conditions they employed, and a value of $\Delta T = 54$ K was reported. A mechanism based on "excess dipole energy" was proposed wherein the localized energy (temperature) of the dipole groups is higher compared to the

TABLE 2: Examples of Changes in Activation Energies and Pre-exponential Kinetic Factors between Conventional and Microwave Synthesis

reaction	MW reaction temp (K)	MW/conv. pre-exponential ratio	microwave act. energy (kJ/mol)	MW/conv. act. energy ratio	ref
NaA zeolite synthesis	353,358,368	1.3×10^5 (nucl.)	118 nucleation	2.36	43,44
		1.6 (growth)	114 growth	1.43	
colloidal silica synthesis	435, 295	2.2×10^{-4}	12 (pH 2.78)	0.29	36,45
aluminia sintering	1323−1873	3.15	85	0.16	37
Al_2O_3/0.1% MgO sintered at 28 GHz	1173−1573	10^{-11}	170	0.30	46
imidization of a sulfone/ketone group	403, 423, 448	1.85	55	0.52	31
polymn. of ε-caprolactone	423−503		23	0.42	47
ethylacetate synthesis	343, 353	5.3×10^{10}	11	0.06	48
PEPA-3-4-ODA	573, 603	5.2×10^{-4}	116	0.68	49
PETI-5 polymer cure	573, 603	3.2×10^{-6}	72	0.51	49

nonpolar bonds within these systems. These authors also propose that pulsed microwave energy would produce effects different from those produced by continuous exposure.

In 1994 Bush and Methven[32] described a nonequilibrium temperature reaction (NETR) theory for the rate enhancement for polymerization using microwave heating. The argument was that one polymerization initiator was more susceptible to microwave heating, and its, "effective [initiator] temperature will be higher than the measured bulk temperature". The result is "rate... enhanced up to 20 times...".

Table 1 summarizes the temperature variations (ΔT_μ) and the corresponding change in enthalpies reported in the literature for various systems heated by microwaves. These macroscopic variations in temperature can be up to 100 K.

2.2. Microwave Effect on Activation Energy, $E_{a\mu}$. The activation energies for specific reactions heated by microwaves have been reported, and these can significantly differ from those reported for the conventional syntheses. The energy variation exists because of the differences in dielectric properties of the reactions, intermediates, and products, allowing for selective heating.

Typically, the reported activation energy decreases under microwave heating compared to conventional heating. For example, Falamaki[36] reported an activation energy of 12 kJ/mol for colloidal silica growth under the influence of microwaves. This is significantly lower than that reported for conventional synthesis (>41 kJ/mol). Lowering of the activation energies has been observed for other systems, including ceramic sintering,[37] polymer curing,[38,39] and organic synthesis.[40−42]

Gizdavić-Nikolaidis and Adnadjević'[43] reported the activation energy calculated for NaA zeolite formation under microwave heating. Unlike most other reports, their estimated activation energies for nucleation and growth are greater than those observed for conventional synthesis (respectively 50 and 80 kJ mol^{-1}). They describe the main process that influences the kinetics of NaA crystallization in a microwave field as the formation of an aluminosilicate complex from the precursor liquid during the release of hydrated Na^+ ion from the hydrogel. The mechanism is explained as a fast activation of a "primary structural motive" (hydrated Na^+ ion). Microwaves can energize specific components (Na^+) in the reaction; this affects the kinetics of the overall reaction. Thus, the pre-exponential kinetic factor more than compensates for the increase in activation energy (see below). Examples of the difference in activation energies for reactions using conventional versus microwave heating from the literature are shown in Table 2.

Table 2 also shows the differences in pre-exponential factors for the microwave versus the conventionally heated processes. These are calculated from the differences in rate and changes

due to the activation energies that are presented. It is obvious that these changes in pre-exponential factors are significant. We will combine the transition entropy contribution and more conveniently (and possibly more realistically) compare the free energy profiles of the reaction coordinates.

2.3. Changes in Activation Energy or Effective Temperature? The proposed changes in temperature or in activation energies due to microwave exposure in sections 2.1 and 2.2 above were most often estimated from differences in reaction rates as interpreted with an Arrhenius expression. In each case, the other variable (ΔT_μ or $E_{a\mu}$) was assumed to be constant. What is the relation between an effective temperature and the equivalent change in energy levels for the interpretation of changes in reaction rates? From absolute reaction rate theory or, as simplified in the Arrhenius equation, the reaction rate constants can be represented in terms of the Gibbs free energy or the activation energy between the reacting and transition states, respectively. Pre-exponential factors a or A account for transition probabilities and the transition entropy in the case of the Arrhenius eq 1.

$$\text{rate constant} = a_e{}^{-\Delta G^*/RT} = A_e{}^{-E_a/RT} \tag{1}$$

The ratio of reaction rates for different activation (or Gibbs transition) energies at the same temperature can be expressed assuming that the pre-exponential factor, a, is the same when the transition Gibbs free energy is employed.

$$\frac{\text{Rate}_1}{\text{Rate}_2} = e^{-[\Delta G_1^* - \Delta G_2^*/RT]} = \frac{A_1}{A_2} e^{-[E_{a1} - E_{a2}/RT]} \tag{2}$$

If the energy profile is the same but the temperatures change, $T_1 \rightarrow T_2$, then the rate ratio could be expressed with constant pre-exponential factors.

$$\frac{\text{Rate}_1}{\text{Rate}_2} = e^{-[\Delta G^*/R][1/T_1 - 1/T_2]} = e^{-E_a/R[1/T_1 - 1/T_2]} \tag{3}$$

If $\Delta G^* = \Delta G_1^*$ and $T_1 = T$, then

$$\frac{\Delta G_2^*}{\Delta G_1^*} = \frac{T_1}{T_2} ...or... \frac{E_{a2}}{E_{a1}} = \frac{T_1}{T_2} \tag{4}$$

Thus, a change in the effective temperature can be analyzed as if there were a change in the relative energies either of the transition states or of the relative energies of intermediates.

Prior analyses of the influence of microwave exposure have alluded to and/or proposed differences in temperature due to exposure to microwave radiation (Table 1). These analyses show

that an equivalent kinetic or equilibrium analysis can be conducted by analyzing activation energy or free energy differences between different states. These changes in free energies are examined in these analyses. This would mean a 100 K temperature change from room temperature is equivalent to a 25% change in activation energy.

2.4. Enhancement at Interfaces. Interfacial reactions are particularly susceptible to microwave influences. Maxwell–Wagner interfacial microwave polarizations are well documented[50–52] phenomena that occur for heterogeneous systems. Simple systems with known geometries and differences in dielectric properties can be analyzed to demonstrate that the interfaces between materials with differing dielectric properties provide loci for microwave interactions. Adsorption of a high dielectric adsorbent on a surface provides two significant new interfaces: between the vapor phase and the sorbed phase, and between the sorbed phase and the solid surface. Species sorbed (or formed) on a surface are more susceptible to microwave interactions.

The adsorbed species involved in a catalytic reaction sequence may have different abilities to absorb and interact with a microwave field. Our studies of adsorption in the presence of microwaves demonstrated that sorbed species with different permittivities exhibit different *effective temperatures*.[5] This effective temperature is directly related to the permittivity of the sorbing species and the instantaneous microwave power. As shown above, a change in the energy level of the intermediate species[5] is kinetically equivalent. As reaction intermediates associate, dissociate, and/or rearrange their bonds, their abilities to absorb microwave energy can change significantly, for example, when polar bonds are formed or broken at an intermediate reaction step. Thus, microwave exposure can change the relative energies of the intermediate species in a sequence. Changing the intermediate energy levels in a reaction sequence will certainly influence the overall kinetics (as with using different catalysts). How significant an impact will a change in a single energy level have on the overall kinetics?

While it is impossible to quantify individual molecular temperatures, the amount of sorbate adsorbed in the presence of microwave exposure can be quantified. While a surface temperature might not be measurable or relevant, how microwave exposure influences the amounts and concentrations of surface species would be very relevant to kinetics. An "effective temperature" of the adsorbed phase during adsorption in the presence of microwaves can be found by relating conventional adsorption isotherms to isosteres obtained in the presence of microwaves. Equating the adsorbate pressure required to achieve a specific coverage (an isostere) in the presence of microwave irradiation to the amount adsorbed for a conventional isotherm allowed for an estimate of the effective surface temperature in the presence of microwaves. The energetics and/or the "effective temperature", T_{eff}, of individual species at interfaces can be changed by exposure to microwaves. The "effective" temperature is a steady-state condition that represents absorption balanced with heat transfer by conduction, convection, and radiation.

The "effective" surface temperature increased with the bulk liquid permittivities for adsorbates having a higher permittivity for a particular adsorbent and surface coverage (θ) and with the microwave power applied. The effective temperature also increased with increasing the microwave power for a particular adsorbent, adsorbate, and relative pressure studied,[5] and therefore is a function of these parameters, as shown in eq 5.

$$T_{eff} = F(\theta(P), E^2, \epsilon''(T), T_{ex}) \qquad (5)$$

with variables θ, the surface coverage (a monotonically increasing function of P, pressure); E^2, the microwave power (related to the square of the microwave electronic field intensity, E, and often a function of position and time); ϵ'' (the local imaginary component of the permittivity reflecting conversion to heat; ϵ'' is a function of temperature); and T_{ex}, the external temperature. The effective temperatures differ greatly for each sorbed species from less than 1 K to more than 100 K above the ambient temperature. Several results from our experimental studies of "effective" temperatures are listed in Table 1, above.
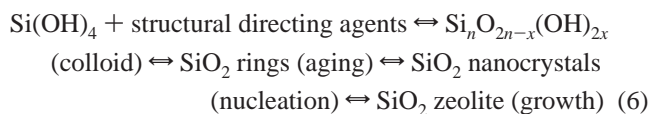
3. Approach

The current hypothesis differs significantly from prior suggestions for the enhancement of reactions due to microwave exposure for interfacial systems. We have documented[53] that the effective heating depends not only on the spatial, volumetric variation in the E-field due to microwave exposure, but that it also depends on the properties of specific species sorbed onto the surface, i.e., at the interface.

Chemical reactions involve a sequence of intermediate species, that is, a reaction mechanism. For heterogeneous reactions, the reactants rearrange or adsorb at an interface for all but the simplest of reactions. Molecules associate with surfaces or solvent species; dissociation and/or bond rearrangement can occur. Most commonly, the mechanisms are envisioned to involve at least three steps. Heterogeneous catalytic reactions are, as an example, perceived to involve the following sequence: adsorption of the reactant(s); at least a single reaction step on the solid surface; and desorption of the products. A rate-controlling step is usually assumed to simplify the kinetic analysis, from which an analytical solution can often be derived.

If the effect of microwave exposure would be to lower the activation energy for a single rate-controlling step in a process, then the rate of the process would probably increase (as documented in Table 2). The same argument would apply if microwave energies would lower the highest intermediate transition state energy in a sequential reaction, just as a better catalyst is perceived to provide a sequence of lower energy states for a reaction.

However, if the effect of microwave energy did not change (or even increase) the highest intermediate transition state energy relative to the reactants in a sequential reaction, it is not obvious how the rate would change. If there is no single rate-controlling step, the influence is even more complex. Such a sequence might exist for synthesis processes. As an example, zeolite synthesis is perceived to proceed by a sequence of reversible steps, viz:

$$Si(OH)_4 + \text{structural directing agents} \Leftrightarrow Si_nO_{2n-x}(OH)_{2x}$$
$$(\text{colloid}) \Leftrightarrow SiO_2 \text{ rings (aging)} \Leftrightarrow SiO_2 \text{ nanocrystals}$$
$$(\text{nucleation}) \Leftrightarrow SiO_2 \text{ zeolite (growth)} \quad (6)$$

3.1. Methods. We performed a kinetic simulation to evaluate the potential influence of microwave exposure to the overall reaction kinetics. We chose a simple sequence of first-order reversible reaction steps to test the influence of microwaves. Also, for simplicity, we will manipulate the relative energy of a single reaction intermediate and the associated transition states by which this intermediate is created or reacts further within the sequence. Our "base case" was chosen as a sequence of three reaction intermediates (Reactant $\rightleftharpoons RI_1 \rightleftharpoons RI_2 \rightleftharpoons RI_3 \rightleftharpoons$ Product, with reaction intermediates RI_{1-3}).
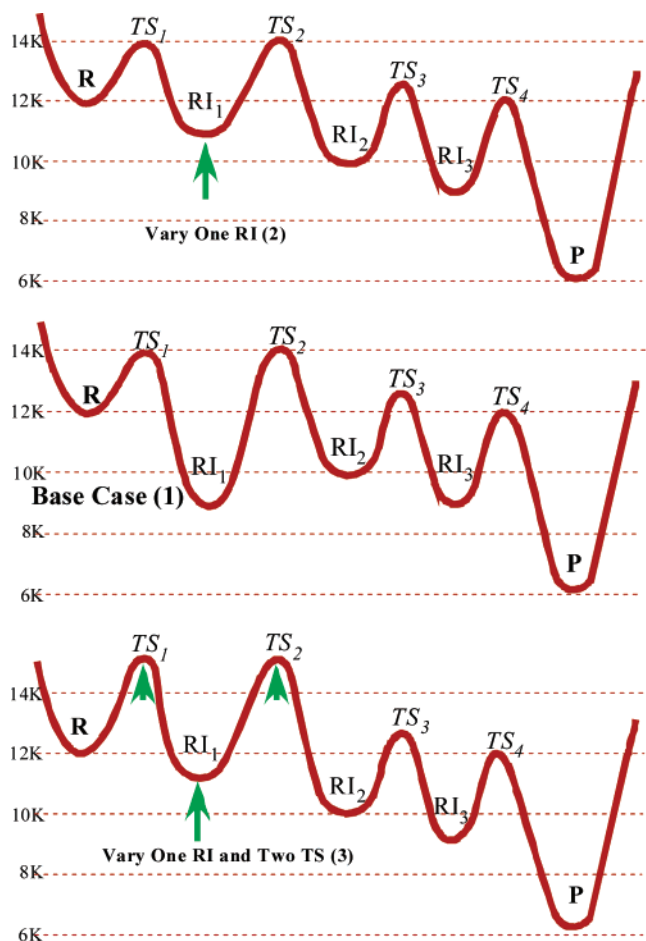
Figure 1. Schematic of the (free) energy transitions of a hypothetical first-order chemical reaction sequence involving three intermediates. Center: base case, R = reactant, RI_{1-3} = reaction intermediate, P = product. Top case: #2, intermediate RI_1 is raised in energy. Bottom case: #3, both intermediate RI_1 and associated transition states (TS_1 and TS_2) are increased in energy.

The base case (1) is chosen with the first reaction intermediate relatively strongly adsorbed, as might occur with polar bonds being formed (and, thus, is potentially susceptible to microwave influence). The reaction coordinate for this base case is represented in Figure 1 (center).

Two reaction energy coordinate changes are analyzed: in Case 2, the highest intermediate transition energies are unchanged, while the energy (temperature) of the relatively strongly bound single intermediate state is raised; in Case 3, the highest adjacent intermediate transition energies are raised, and the energy (temperature) of a single intermediate state is raised. In Case 3, the Evans−Polanyi relationship between the enthalpy differences between intermediate species ΔH_{react} and the activation energies E_a was assumed, i.e., eq 6.

$$E_a^{mw} = E_a^o - p(\Delta H_{react}^0 - \Delta H_{react}^{mw}) \qquad (7)$$

where the Evans−Polanyi constant is assumed to be $p = 0.5$.[54] The superscripts "0" and "mw" designate the base case and the reaction under microwave exposure, respectively.

In order to incorporate the measured changes in preexponential factors documented in Table 2, we base our simulation profiles on the free energy profiles, not energy or enthalpy profiles. The free energies of the species employed in the simulations are listed in Table 3.

TABLE 3: Relative Free Energies ($\sim$kcal/mol/1000) of Reaction Intermediates (RI_{1-3}) and Transition States (TS_{1-4}) for the Various Reaction Coordinate Cases Analyzed

simulation	R	TS_1	RI_1	TS_2	RI_2	TS_3	RI_3	TS_4	P
Case #1 (base)	12	14	9	14	10	12.5	9	12	6
Case #2	12	14	11	14	10	12.5	9	12	6
Case #3	12	15	11	15	10	12.5	9	12	6

The relative energies of Cases 1 (base), 2 (energy increase of RI_1) and 3 (increase in RI_1 and transition states 1 and 2) are shown in Figure 1 with the base in the center, 2 above, and 3 below.

The sequential reaction was simulated employing Monte Carlo methodology for 4000 time increments. The numbers of species transformed from each relatively stable species (R, RI_1, RI_2, RI_3, and P) by forward and reverse reaction were calculated for each time increment by the relative free energies of the individual species and the transition states between the species. In each simulation, a series of reaction intermediate and transition states relative free energies was assumed (Table 3; Figure 1). Each reaction step, both forward and reverse, was assumed to be first order. After each step, the numbers of species formed or lost from each intermediate species are accounted for to calculate the number present after the time step. Similar calculations are then performed with the new concentrations for the next time step.

The time increments used here have no meaning outside the framework of a specific reaction. A reaction that takes 1 h to achieve 90% conversion in the base case would be represented by a time increment of slightly less than 1 s, while a 1 min reaction would involve a $\sim$0.01 s increment.

We initially analyzed the changes in the overall reaction rate due to constant changes in the reaction profiles for each case, 1−3. This assumes that the microwave exposure and related changes in the reaction profile or individual temperatures do not vary. In reality, the changes due to microwave exposure are not constant in time or space.

3.2. When Microwave Exposure Varies. Changes in chemical reactions due to microwave exposure have been demonstrated in a variety of reactor configurations. Most studies have been conducted in a multi-mode cavity such as the common microwave oven. These do not represent constant exposure to microwave radiation of constant intensity. Since the cavity dimensions are not simple multiples of the wavelength, the instantaneous microwave intensity in a multi-mode cavity varies periodically with a complex combination of harmonics. Reactions conducted in waveguides also do not necessarily represent constant exposure to microwave excitation. Microwave exposure in contrast to conductive heating provides almost instantaneous direct interactions with species in a system. Thus, the exposure can vary significantly in intensity with time and space as the reaction proceeds. It is thus necessary to understand the influence of microwaves on reaction sequences if the intensity varies periodically. Is the net result an average of the extremes, or does it favor the more efficient route for microwave perturbation of energy profiles?

Pioneering studies by Douglas et al.[55] and Laurence et al.[56] have analyzed the potential enhancements due to periodic concentration perturbations of complex chemical rate processes by conventional means. By implication, similar enhancements would occur for variations in pressure or temperature. They have demonstrated that the nonlinear nature of reaction rates favor the faster processes during periodic variations.

To simulate the variations of a multimode cavity, we analyze a periodic variation between reaction profiles, i.e., between the
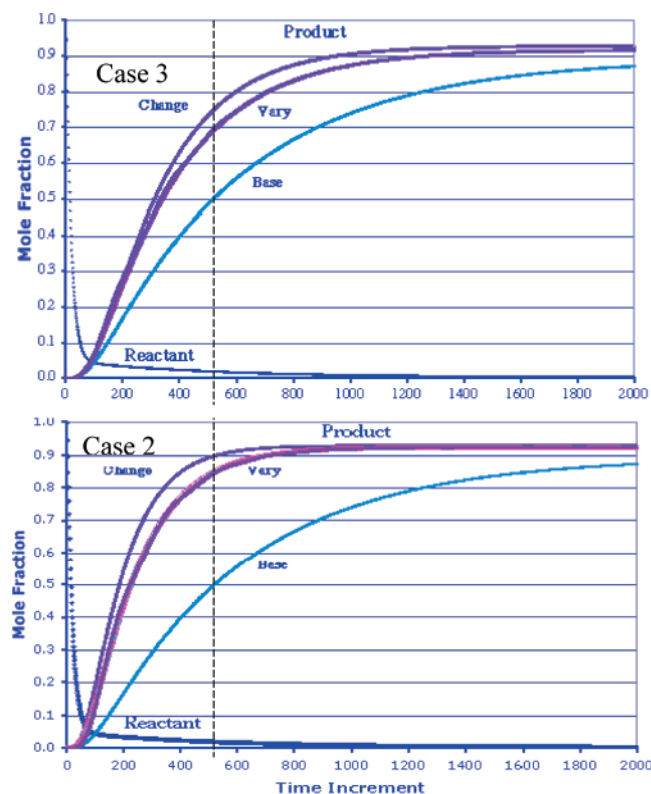
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Figure 2. The products formed in the base case and those for changes in the reaction profile due to microwave exposure in Case 2 (bottom) and 3 (top). Finally, the product formation for a periodic variation between the two profiles at a frequency of 10 or 2 (relative to time increments) are also shown as "Vary". The dashed line is added for comparison.

base case and Cases 2 and/or 3. The variation frequency is related to the time increment such that the period of the variation is $360/f$, where the frequency is f.

The resultant instantaneous activation energy, Ea(t) for a variation between the base case (Case 1, Ea_b) and the changed cases (Cases 2 or 3, Ea_c) are related to the time increments, t_i, and the frequency, f, by the following eq 8, viz.:

$$Ea(t) = Ea_b + (0.5 + \cos((t_i \cdot f \cdot \Pi/180)/2) \cdot (Ea_b - Ea_c)) \quad (8)$$

The numbers of species converted are then calculated at each time increment for each forward and reverse reaction (based on the instantaneous activation energies and temperature). These changing reaction profiles are employed to determine the numbers of species present for the next time increment.

4. Results and Discussion

The formation of product and the decrease in reactant concentrations for the base case and microwave perturbed Cases 2 and 3 were analyzed. These are compared to periodic variation between the base case and Cases 2 or 3 in Figure 2. Sinusoidal variations of the energy for the first reaction intermediate between the two respective free energy profiles were analyzed as shown in eq 8, above. Figure 2 shows the reactant decrease, while the products from Cases 1 (base) and 2 (bottom) or 3 (top) and a variation between the two reaction coordinates are shown. The increase in the relative energy of the first intermediate (RI$_1$), due to microwave exposure, results in a significant increase in the rate of product formation. An order of magnitude increase in the rate of product formation can easily result. A variation between the two reaction coordinates most closely
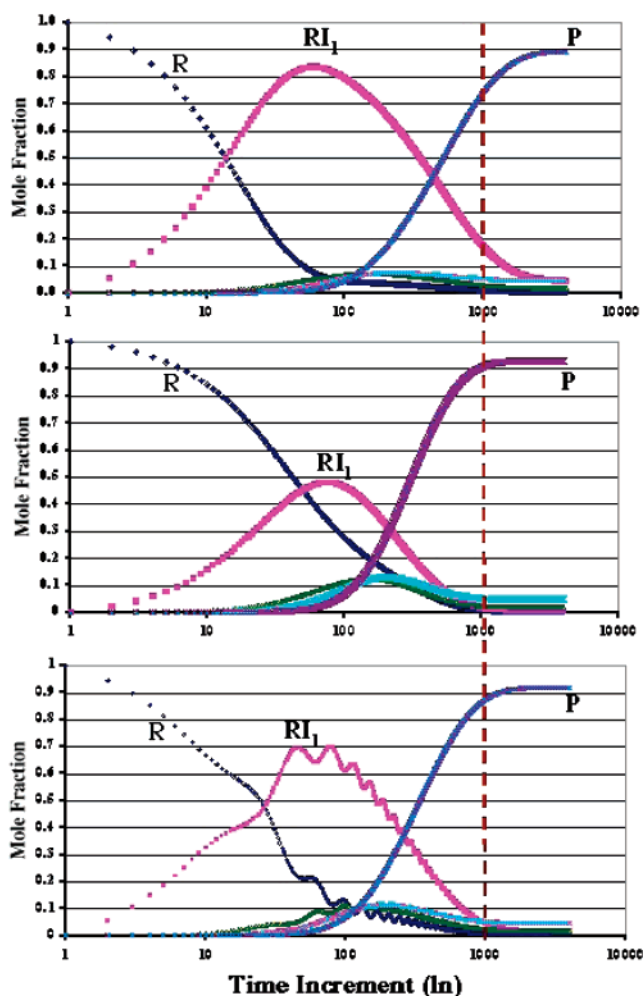

Figure 3. Profiles of the reactant, reaction intermediates, and product in the base case (top), the modified Case 3 (center), and the variation case (bottom) as a function of time (on a log scale). The line at 1000 time increments facilitates product formation comparison.

follows the more favorable reaction pathway (Cases 2 or 3 compared to Case 1) as the reactants and intermediates find the easiest route toward the lowest energy state. The nonlinearity of the reaction kinetics contributes to this. This enhancement is not a significant function of the frequency of variation between the two reactions coordinates. Indeed, the "Vary" curves in Figure 2 represent variation frequencies of 2 and 10 (see above), and the reaction rates in both cases are nearly identical. This is consistent with the prior studies of Douglas and Rippin,[55] Bailey and Horn,[57] and Laurence and Vasudeva,[56] wherein significant reaction enhancements are evident under both low and high perturbation frequencies.

The progress of the reaction is mapped with concentrations of the reaction intermediates with time for the base case and is shown in Figure 3 (top). The first intermediate, RI$_1$, exhibits the highest intermediate concentration as it is the first to form and has the deepest energy well (i.e., the most relatively stable).

The more interesting (and challenging) case is when both the intermediate and the associated activation energies are increased as in Case 3 (see Figure 1, bottom). The changes in the relative energies of the reaction intermediates are readily seen in Figure 3 (center). Now the relative concentration of RI$_1$ exhibits a reduction of over 40%. The other reaction intermediates are more plentiful, and the product is formed more rapidly, even though the maximum activation energy has increased along
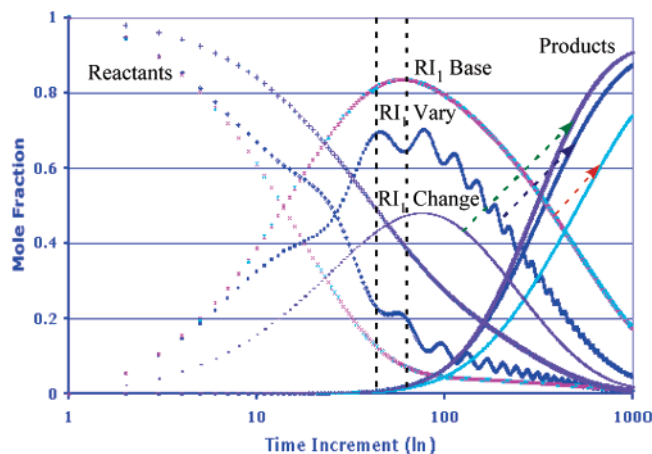
Figure 4. Comparison of the reactants, products, and reaction intermediate (RI₁) for the (base) reaction coordinate, reaction coordinate 3 (change), and a periodic variation between these two coordinates at a period of 10 time increments. The dashed lines are employed for comparison between these in the text.

this reaction coordinate. Reaction intermediate 1 is effectively being "pumped" over the barrier by exposure to microwaves.

Periodic variation between the two reaction coordinates, a possible consequence of exposure to a variable microwave field, is shown in Figure 3 (bottom). The first reaction intermediate is evident as a transient species between the base and the changed coordinate cases. The "ripples" in concentrations are due to the periodic variation between the two coordinates. The product is formed, however, almost as rapidly as it is in the purely changed Case 2. The overall reaction rate greatly favors the most facile path (or paths) when the reaction is periodically varied between intermediate reaction coordinate profiles. Such a preference would be exhibited for other variations between favorable and less favorable reaction coordinates. This is due to the exponential dependence of rate on energy differences (or effective temperature).

Direct comparisons of the changes in reactant, product, and first reaction intermediate concentrations for the three variants are shown in Figure 4. The changed reaction coordinate exhibits a delay and reduction in the maximum for the first reaction intermediate (see crosses). Yet, the product is produced more rapidly, almost as rapidly as when there is a periodic variation between the two reaction coordinates. The behavior of the reactant and the reaction intermediate for this simulation suggest a reason for microwave rate enhancements. Reaction intermediate 1 decreases rapidly between the dashed lines, while the reactant concentration varies little. This represents "pumping" of this reaction intermediate over the barrier toward the products as the relative transition state energy for the forward reaction is decreased.

The progress of the reaction with Case 3 is more sensitive to the frequency of variation between reaction coordinates than for the simple increase in a single reaction intermediate energy for Case 2 compared to Case 1, in Figure 4.

The two most unusual behaviors that arise as a result of the rate of variation between the unperturbed profile and that for modified profiles are demonstrated in Figure 5. The influence of the product concentration as a function of the frequency of variation between the two reaction coordinates is shown in Figure 5 (top) compared to the base and modified reaction coordinates of Case 3. The product concentration can indeed be larger in the variable case than either the base or change reaction coordinates at low conversions. The influence of variations in the energy coordinate at the first reaction inter-
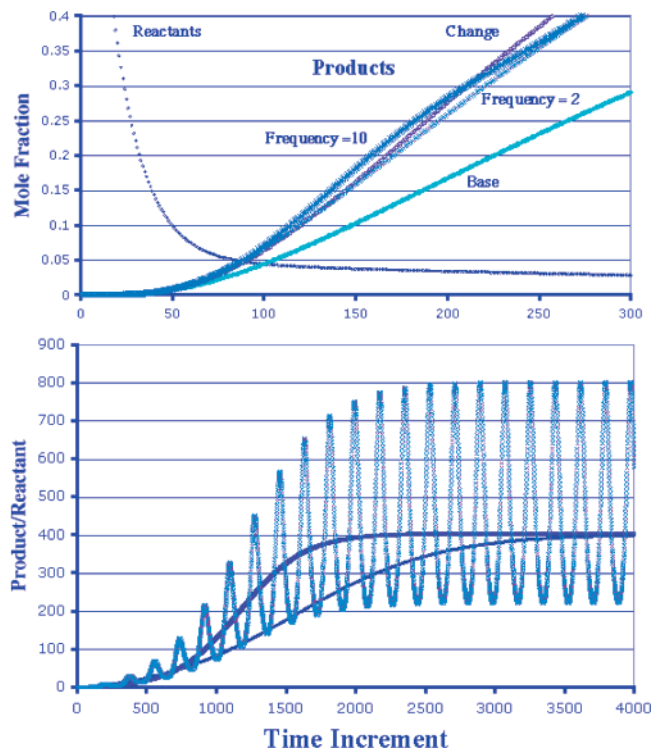

Figure 5. The concentration of reactant and product for the base case, Case 3 (change), and a periodic variation between these cases at different frequencies (top). The instantaneous ratio of product to reactant as a function of time for the base case, Case 3, and a variation between these two coordinates at a frequency of 2.

mediate becomes less pronounced as the conversion increases. Again, this unusual enhancement is frequency-dependent.

The equilibrium concentration ratio of product to reactant for all of these reaction coordinates is the same, i.e., 400, with these free energies. However, the instantaneous ratios of product to reactant can change as the reaction progresses and the concentrations of intermediate species change. Under normal reaction conditions, there is a monotonic increase from a product-to-reactant ratio of 0 to the equilibrium ratio. As seen in Figure 5 (bottom), a variation between two (or more) reaction coordinates can perturb the ratio of the concentrations of reactants, intermediates, and products. The species then attempt to achieve instantaneous equilibria between the pairs of adjacent states. In effect, more reactant can be transformed to the first reaction intermediate than would be present with the unmodified reaction coordinate. This effect means that variations between reaction coordinates can result in instantaneous reactant or product ratios that exceed those dictated by equilibria for conventional reactions.

The examples of reaction coordinates simulated above were chosen as simplified modifications. Herein, we analyzed the relative changes in a single intermediate in a sequence wherein the largest activation energy does not decrease as a result of microwave exposure (which would be an obvious increase in rate). These changes in reaction profiles (increases in effective temperatures) yield over an order of magnitude increase in the overall reaction rate. The overall reaction rate depends intrinsically on the relative energies of the sequence of intermediates. More complex (realistic?) changes in the relative intermediate and transition reaction energetics could yield even more dramatic increases in reaction rates; however, they could also result in decreases in the overall reaction rate. If, for example, microwave exposure decreased the coverage of a reactant species, the reaction rate could decrease. Thus, it might be less likely to

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react on the surface (as we have found for NO_x conversion on auto exhaust catalysts[58]).

These studies and analyses have provided a basis for understanding experimental observations associated with microwave enhancement of interfacial reactions. Microwave energies can selectively vary the relative intermediate energies of species in a reaction sequence. This manipulation of intermediate reaction energy states can control and enhance reaction rates.

These analyses further suggest that other variations in microwave exposure during chemical reactions (e.g., different or variable frequency or power) might be employed to provide novel control and reaction enhancements for many (but not all) reactions. Variations between intermediate energy coordinates can favor a different path within a reaction sequence.

These reaction enhancement phenomena will be greatest when the reaction media is essentially transparent to microwave exposure while the interfaces in the system provide foci for energetic manipulation, i.e., at the reacting (catalytic or synthesis) surface.

These analyses have only considered the net effect of changing the reaction coordinate energy profile without identifying the specific mechanism for microwave interaction. Indeed, microwaves might interact more strongly at a metallic site or with a sorbed species or some complex combination within the reaction intermediate sequence. Microwave theory and simulation will certainly be needed to help, whereas it might be more difficult to capture individual transient species changes by conventional in situ spectroscopy.

5. Summary and Conclusions

One answer to the question, "*How do microwaves influence chemistry at interfaces?*" is that microwaves can change the relative energies of reaction intermediates in a given sequence. We have demonstrated that microwave exposure can change the "effective temperatures" or, equivalently, the relative energies for individual sorbing and sorbed species. The overall reaction rate for a sequence of metastable intermediates in a reaction mechanism can be increased significantly, easily by over an order of magnitude, even if the activation energy maxima do not decrease. In a similar manner, microwaves and their variation could influence other processes comprising a sequence of metastable energy states, such as "configurational" diffusion in porous media. Adsorbed species are particularly susceptible to this influence. However, the manipulation of intermediate states in a reaction sequence does not necessarily depend on interfaces being present. Similar kinetic manipulation by microwaves could even apply for homogeneous reaction media comprising intermediate species with differing susceptibility to microwave energy.

The kinetic consequences for a series reaction due to changes in the effective temperature of a single reaction-intermediate species were simulated. The following conclusions can be drawn from these simulations.

1. Increases in the relative effective temperatures of reaction intermediates due to exposure to microwaves can increase the overall reaction rate by orders of magnitude with photon energies much less than those required to break specific bonds.

2. The reaction profile does not need to be changed permanently to produce enhancement (i.e., increase in the rate), because periodic variation between two reaction profiles tends to exhibit rates dominated by the faster process.

3. Variation of reaction intermediate energies can give rise to greater overall reaction rates than either reaction path alone at moderate conversions.

4. Product/reactant ratios can exceed those normally attainable during the periodic energy variations of the reaction intermediates. The effect depends on the frequency of variation.

It is not necessary to absorb sufficient energy to break chemical bonds in order to have a significant influence on a reaction rate. Stuerga and Guillard[59,60] have correctly pointed out that microwave energies are not large enough to break chemical bonds. Changes in the intermediate energy states in a reaction sequence are found to change the reaction kinetics significantly at energies far below those required to break specific chemical bonds. Indeed, the ability of microwaves to manipulate intermediate energies within the context of a given reaction sequence could lead to significant rate enhancement without changing the mechanism.

It would be possible to capitalize on this ability to manipulate intermediate reaction state energies in several ways. First, these methods could be applied to large-scale processes, wherein the medium is essentially transparent to microwaves (such as many oxide-based catalysts and sorbents). Second, periodic variations in microwave power and their influence on chemical reactions could provide knowledge about the relationship between the reaction rate dynamics, just as "frequency response" methods are employed in control theory or diffusion analyses.[61] Characteristic reaction times would be evident at the period of the power variations.

Reactions at interfaces often require far less energy (occurring at lower temperatures) than their homogeneous analogs. In a similar manner, ultrasound or forms of (electromagnetic) energy could influence the local effective pressures or temperatures and result in rate enhancement.

This explanation of how microwaves can enhance reaction rates does not exclude the other explanations for microwave enhancement as suggested in I–VI, above. Overall reaction rates can often be increased by several different methods (new catalysts, pressures, temperatures, reactor configurations, transient behavior, etc.). This explanation is, however, supported by experimental observation[5] and should be considered.

One advantage of microwave enhancement might then be that microwaves provide sufficient energy to enhance reaction rates by manipulating the relative energies in a specific reaction sequence but less energy than would result in a change in mechanism, e.g., on catalytic or reacting surfaces. However, the relative energy profile does not have to be changed permanently to have a significant effect.

We propose that the most significant influence of microwave enhancement of chemical reactions is that microwaves can change the reaction profile (or relative temperatures) instantaneously and often periodically. These changes are due to the significant differences in microwave absorption by molecular species, particularly at interfaces. Microwave exposure can thus increase reaction rates significantly by periodically providing a more favorable reaction coordinate (selective heating: changing the reaction profile).

Further, the proposed controlled manipulation of microwave exposure cannot easily be interpreted in a multimode reactor such as an oven. Waveguides are required with careful microwave reactor engineering to test and control the microwave exposure in time and space. However, microwave enhancement would often be more evident in a multimode cavity wherein favorable reaction paths might be present even for short times, as the overall reaction kinetics would favor these paths.

Finally, two burning questions have pervaded prior discussions of microwave enhancement in chemistry: "Is there a microwave effect?" and "Is it athermal?".

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Our explanation certainly suggests that microwave enhancement depends on the relative changes in energies (effective temperatures) for intermediates in a given reaction sequence. Microwave energy can influence these relative energies while not transferring the energy necessary to change the mechanism, potentially an advantage. This suggests there is a microwave effect. This effect would depend on frequency and/or its variation. However, the absorption bands (frequency range for absorption) are broad in the fluid and solid states. Thus, we suggest that there is a "microwave effect" for this enhancement mechanism that could be a function of frequency.

The "thermal" (temperature) dependence of this proposed mechanism for microwave enhancement depends on how one poses and interprets the question. Our explanation is based on an experimental "effective" temperature or the relative energies for intermediate species in a reaction sequence. We suggest the pragmatic interpretation of thermality: if less is sorbed (or would be sorbed relative to the gas), the "effective" temperature has increased. The proposed explanation is only locally/molecularly "thermal", otherwise it could be considered athermal.

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