

How Do Microwaves Influence Catalytic Reactions?

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ABSTRACT

Many chemical reactions may be accelerated by order(s) of magnitude due to microwave exposure: considerable energy could be saved. 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 adsorbed species on catalyst surfaces. Changes in the relative energies of reacting species or intermediates are shown to lead to the observed enhancements in reaction rates or selectivities. Moreover, variations in microwave exposure might provide unique kinetic control. A theory for microwave reaction enhancement is established and demonstrated.

Introduction: Microwave Chemistry

The recent American Chemical Society monograph on Green Chemistry(1) recommends to “Use methods that minimize the energy required for a reaction to take place. For example... catalysts or **microwave radiation**...”.

Many catalyst supports are essentially transparent to microwaves; examples are silica, alumina, zeolites and many other oxides. The supported catalytic components often are metallic, 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). Differential heating can require considerably less energy than the conventional heating processes employing conduction and/or convective energy transfer, wherein the whole system including the reaction vessel must be raised to the desired reaction temperature.

This study employed kinetic [Monte Carlo] simulation of the effects of changing the relative energies of intermediate states for an interfacial (Catalytic) reaction. Reaction profiles wherein the overall activation energy did not decrease due to microwave exposure were analyzed. We also analyzed the practical periodic variation of microwave exposure as occurs in an oven or can be induced electronically.

RESULTS 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. This is based on experimental studies as we have demonstrated that microwave exposure can change the “effective temperatures” and, thus the relative energies for individual sorbing and sorbed species(3,4). The reaction rate for a sequence of meta-stable intermediates in a reaction mechanism can be increased significantly even if the activation energy maxima do not decrease, easily by over an order in magnitude. In a similar manner, microwaves and their variation could influence other processes comprising a sequence of meta-stable energy states as an example, interface transport such as “configurational” diffusion in porous media, etc. Interfaces are particularly susceptible to this influence. 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 temperature of reaction intermediates due to exposure to microwaves can increase reaction rates by orders of magnitude at a fraction of the energy required to break specific bonds.
- 2- Periodic variation of reaction intermediate energies will (most often) be dominated by the most favorable energy pathways.
- 3- Variation of reaction intermediate energies can give rise to greater overall reaction rates than either reaction path at moderate conversions.
- 4- Product/reactant ratios can exceed those normally attainable during the periodic manipulations 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 kinetics. Stuerger and Gaillard(5,6) 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 significantly change the reaction kinetics 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 surface reaction sequence could lead to significant rate enhancement.

This explanation of how microwaves can enhance reaction rates does not exclude the other explanations for microwave enhancement: rapid heating etc.. Overall reaction rates can often be increased by several different methods (new catalysts, pressures, temperatures, reactor configurations, transient behavior, etc.).

One advantage of microwave enhancement might then be that microwaves provide sufficient energy to enhance reaction rates by manipulating the relative energies in a reaction sequence but less energy than would result in a change in mechanism.

Finally, two burning questions have pervaded prior discussions of microwave enhancement in chemistry: “*Is there a microwave effect?*” and “*Is it athermal?*”. This analysis will directly address these questions.

Significance

Our ability fully to employ microwave energy to enhance catalytic reactions has heretofore suffered from an understanding of the reason(s) for the enhancement. This paper demonstrates the consequences of our experimental results for adsorption measurements in the presence of microwaves(3,4) on the influence of microwaves on catalytic and other interfacial reactions.

References

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