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Microwave heating as a new way to induce localized enhancements of reaction rate. Non-Isothermal and heterogeneous kinetics.

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Abstract: In this paper we investigate non-isothermal kinetics induced by microwave heating particularly in term of spatial distribution of temperature. We clearly show that it is possible by microwave heating to induce localized superheating (eventually thermal runaway in solid case) which lead to localized reaction rate enhancements.

In a previous paper[1] we have shown theoretically and experimentally potentialities of microwave heating in terms of chemical selectivity induced. These interesting potentialities result from the control of reactive medium heating rate without claiming any specific or athermal effects of microwave heating. Athermal effects have been based on the following hypothesis: for the same temperature of the reactive medium, we observe significant differences in reaction rate between conventional and microwave heating. For reactions with a reaction time close to the heating time, we have forecasted two interesting effects: firstly, a consistent reduction of the reaction time, and secondly in relation to kinetic parameters a selectivity between competitive reactions. These theoretical results have been experimentally proved during the sulfonation of naphtalene. We have shown that it is possible to check an isomeric ratio of 1- and 2-Naphtalene Sulfonic Acids independently of operating conditions such as reactive concentrations. Recently, Herradon et al.[2] have shown similar results in polyols.

In this paper we investigate further non-isothermal kinetic induced by microwave heating particularly in terms of spatial distribution of temperature.

RATE ENHANCEMENTS MICROWAVE INDUCED IN SOLID CHEMISTRY

Several detailed kinetic measurements for homogeneous conditions (with solvents) have indicated that the rates under microwave heating are identical to those observed under conventional heating conditions. Sun et al.[3] firstly concluded that hydrolysis of ATP is faster under microwave heating than under classical heating conditions. Finally their conclusion[4] was that there was no specific activation during hydrolysis of ATP if they took into account thermal gradients within the heated sample. Laurent et al.[5] have shown that the reaction yield and stereoisomer ratios for ene-reactions involving carbonyl enophyles (diethyl mesoxalate with 1-decene and β-pinene, and cyclization of (+) citronellal) are unaffected by the heating mode. Raner et al.[6] have recently shown that the acid-catalysed esterification of 2,4,6-trimethylbenzoic acid in isopropyl alcohol proceed at the same rate for microwave conditions as with an oil bath. More recently, Welt and Tong[7] have shown the absence of non-thermal microwave effects on the thermal degradation of vitamin B1. Then, experimental evidence of specific effects of microwave absorption had not been made with the use of solvent (homogeneous systems with comparative temperature measurements between conventional and microwave heating).

In solid chemistry and in heterogeneous solid-liquid stirred systems (phase transfer catalysis without solvent), many experiments (Barnier et al.[8]) have shown significant differences in reaction rate obtained between conventional and microwave heating. Reaction rate enhancements obtained are higher than those classically obtained with solvents. How can we interpret these results? Some authors have claimed specific effects or athermal effects of microwave irradiation. Until now, even if a few temperature measurements have been made in solvent bulk, no thermal spatial distribution measurements have been made for solids used in organic chemistry (alumina, clays, ...).

In this paper, we will experimentally show the spatial distribution of temperature induced by microwave heating of a powder (alumina). Then, we will theoretically analyse chemical consequences of the localized superheatings in terms of reaction rate enhancements.

TEMPERATURE DISTRIBUTIONS WITHIN SOLIDS

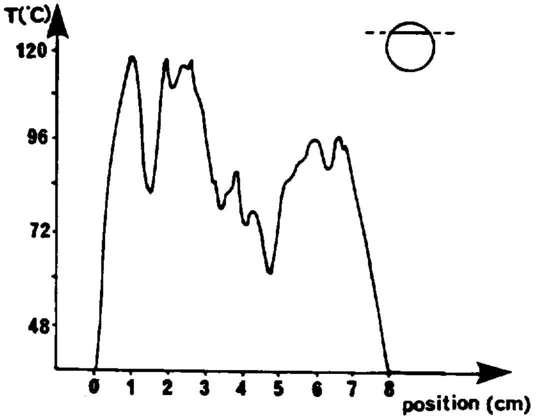
Measurements and estimations of temperature spatial distributions induced by microwave heating are very difficult. The first estimations have been made by indirect measurements (i.e. characterization of products resulting from microwave heating). It is well known that microwave heating of solid materials such as alumina can lead very rapidly to fusion in relation to thermal dependency of dielectric loss[9]. For solid materials, the physical origin of the exponential thermal dependency of dielectric loss usually corresponds to the increase of conduction with temperature associated with thermal activation of electrons. Consequently, most of local thermal fluctuations can be amplified, thus it is very easy in stronger microwave irradiation to obtain local temperatures greater than 1000 °C[10,11].

Direct temperature measurements are very difficult. No wire can be introduced within microwave oven, because it will become an antenna. We must use a fluorooptic thermometer with an optic fiber as a probe. This kind of thermometer is well adapted for measurements within solvents. Temperature measurements usually lead to an average temperature because thermal gradients induce convective motions. Those convective motions lead to a strong stirring with a characteristic time close to a few milliseconds. For solid materials, temperature measurements are very difficult even with conventional heating. The three crucial conditions for a "thermometer" are partly verified. The thermal capacity of the probe should be low (problem for measuring a spot temperature, or a small quantity of material). The thermal resistance should be as low as possible. That means a good contact between the probe and the powder. The time response of the thermometer should be lower than that one from the studied system. For powder, these three conditions are partially verified, and the use of a probe must be limited. Morever, contrary to liquids in which convection lead to stirring, temperature is heterogeneous and we need to obtain spatial distribution of temperature. Infra-red thermography can show the surface temperature distribution without any contact with the studied object. Therefore the infrared thermography is a good choice, despite its surface character (microwave heating leads to core heating, so for thin layer, surface temperature distribution is close to the core temperature of the layer).

We have studied the temperature distribution of alumina associated with potassium acetate. The association of organic reagents with inorganic materials (such as alumina, silica and clays used in "supported chemistry") strongly enhance their capacity to absorb microwaves. Bram et al.[12] have shown that the association of potassium acetate with alumina or silica lead to a reactive medium which strongly absorbs microwave energy. The temperature monitoring becomes very difficult in relation to thermal runaway (temperatures are close to 600 °C after a few minutes of heating). This consistent difference between pure alumina and alumina with absorbed potassium acetate results from a consistent enhancement of dielectric loss.

The alumina powder (1/1000 of potassium acetate) is contained in a Petri box (9,5 cms in diameter with the height of the alumina close to 2 mm) localized in the center of a microwave cavity. This microwave cavity is quite different from domestic microwave oven because the electric field distribution is known and controlled. This microwave cavity has been designed by the authors. An infrared camera (CIRCE) with a frame scan of 2 frames/s is aimed at the alumina surface through a trap constituted of a metallic cylinder. The temperature distribution at 256*100 points is digitized into 8 bits, and we can obtain the temperature distribution along the Petri box. Figure 1 gives results obtained for a microwave power of 200 W, and for a heating time of 30 seconds.

Fig. 1: Temperature profile for alumina (along the Petri box).



The temperature scale has been determined by standardization with a fluorothermometer. Thermal gradients close between 7°C/cm and 70°C/cm have been obtained. This method provides information relating to the spatial distribution whereas the technique of infrared thermography under microwave usually used allows only a spatial mean temperature[13].

LOCALIZED RATE ENHANCEMENT

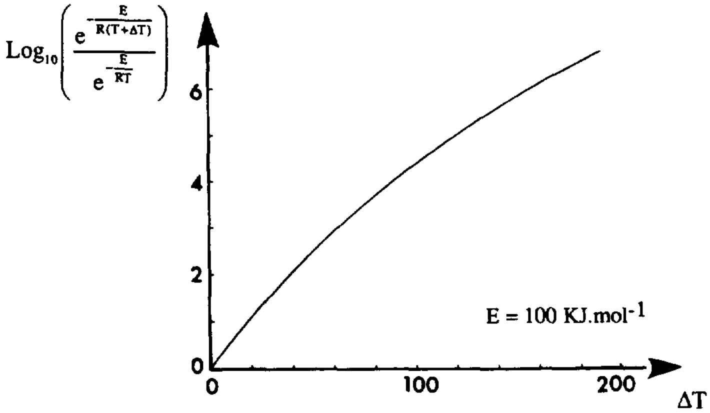
According to our estimation of thermal gradients within powders heated by microwaves, we can estimate chemical consequences of thermal heterogeneities in terms of non-isothermal kinetics. Localized superheatings can enhance significantly the yield of the studied reaction without any significant effect upon the average temperature.

In the following we will consider a kinetic model based on Arrhenius law taking into account spatial and temporal change of temperature in relation to the presence of "hot spots". In fact we consider a simple reaction: two reagents R_1 and R_2 react to product P with a reaction kinetic law whose preexponential factor is k, and whose activation energy is E as described by scheme 1:

$$R_1 + R_2 \xrightarrow{k,E} P$$

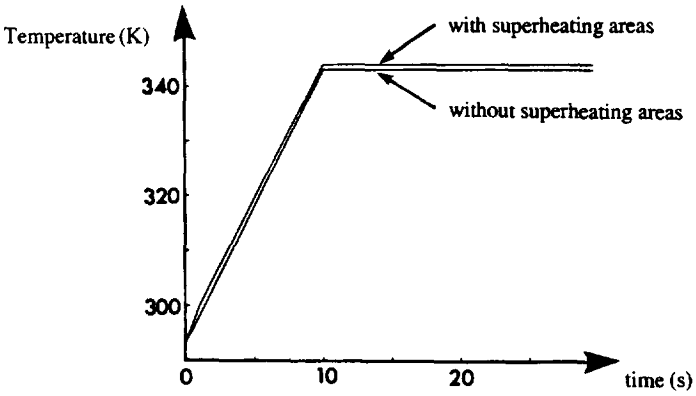
In relation to exponential change of reaction rate with temperature, it is obvious that small changes of temperature can induce consequent changes of reaction rate. Figure 2 describes changes with thermal fluctuation ΔT of ratio of the Arrhenius terms for temperature $T + \Delta T$ and for temperature T.

Fig. 2: Influence of the temperature on Arrhenius term.



A small change of temperature induces a very strong enhancement of reaction rate. In the following, we will consider two temporal profiles of temperature: one for the heated medium, and the other one for the hot areas (hot spots). These two profiles are used as a base for a weighting according to the density of hot spots.

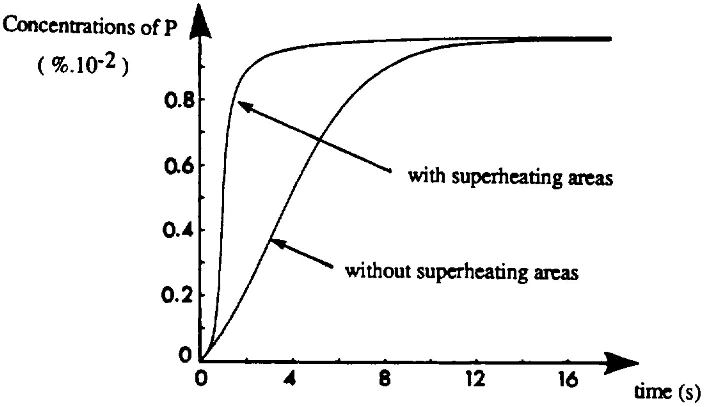
Fig. 3: Average temperature profiles with and without superheating areas.



Heating time has been chosen between 1 second and 10 seconds, and superheating to 70°C. These values agree with our experiments described above. Figure 3 describes the average temporal profile of temperature with and without "hot spots". Population of hot spots is 2 %.

Figure 4 shows consequences in terms of production of P. The kinetic parameters correspond to very realistic values for classical reactions (preexponential factor $k=1.45\ 10^{13} mol^{-1}s^{-1}$, and activation energy $E = 80$ $KJ.mol^{-1}$, initial concentrations of R_1 and R_2 equal to $1\ mol.l^{-1}$).

Fig. 4: Kinetical curves with and without superheating areas.



These results prove that hot spots effects on reaction rate and average temperature have no possible comparison. A very small density of superheating areas is sufficient to induce a consequent rate enhancement, even if their effects are not detectable on average temperature.

CONCLUSIONS: PREPONDERANCE OF THERMAL EFFECTS

According to these results, differences in reaction yield between classical and microwave heating can be explained in terms of localized superheatings. These effects of localized rate enhancement should be obviously consequent for organic syntheses on inorganic solids (alumina, silica or clays). These materials have no intrinsic potentialities of stirring, and thermal properties are not usually able to allow homogenization by thermal diffusion. These forecastings may give a plausible explanation of results obtained by Bram et al.[12] for alkylation of potassium acetate on alumina, and activation of organic compounds absorbed on inorganic solids (such as alumina and clay) obtained by Ben Alloum et al.[13]. This conclusion remains however qualitative because of the lack of comparative thermal data between the two protocols (microwave and conventional).

Since these works, some experimental improvements have been made in reactions using solid-liquid phase transfer catalysis[15,16]. The temperature has been monitored under microwave heating by means of infrared radiothermometry[13]. Then comparative studies between microwave and conventional heating have been conceivable. Despite the same average temperature reaction, significant rate enhancements are observed (microwave yields are largely better than those described under classical heating for a longer time). It seems that the model described above may be an interpretation of these results. In fact, the measured temperature is on one hand, always an average value[13] and on the other hand usually underestimated. For solids and solid-liquid systems, the measured temperature will be always a surface value and so underestimated. This is due to the microwave core heating (thermal gradients are always inverted compared to conventional heating). According to the model, weak local overheats (undetectable on average temperature) are enough to induce consequent rate enhancements.

In conclusion, we believe that "non-thermal effects" claimed by some authors probably result from difficulties relating to temperature distribution estimations, and particularly of local thermal gradients induced by microwave heating.

If the role played by microwave irradiation over collisional or mechanistic term remains unknown and obscure today, it is otherwise for thermal effects. Indeed the specific and the essential interest of microwave heating is its potentialities to induce very strong thermal gradients, and very fast heating rates. Effects of very fast heating rates have been examined in our previous paper. Here, we clearly show that it is possible by microwave heating to induce localized superheatings (eventually leading to thermal runaway in the case of solids) which lead to localized reaction rate enhancement. According to the authors, it seems that microwave heating opens new ways for synthetic chemistry.

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