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THEORETICAL CONSIDERATIONS REGARDING ACTION OF MICROWAVES IN ENVIRONMENTALLY FRIENDLY ORGANIC SYNTHESES

CONSIDERAȚII TEORETICE PRIVIND ACȚIUNEA MICROUNDELOR ÎN SINTEZELE ORGANICE

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Abstract.
Microwave irradiation in chemistry introduced new concepts related to energy absorption and transmission, a completely different phenomenon in conventional heating reactions. The method is environmentally friendly, because in most cases the reaction time is substantially reduced from hours to minutes, the yields are significantly better, the amount in secondary products is diminished, and some syntheses take place in the absence of solvent. Nowadays, microwave irradiation is successfully applied in almost all types of chemical reactions, with delightful results.
Key words: microwave irradiation, modern and efficient alternative, environmentally friendly

Rezumat.
Iradierea cu microunde în chimie a introdus noi concepte referitoare la absorbţia şi transmiterea energiei, fenomen complet diferit în reacţiile cu încălzire convenţională. Metoda este prietenoasă cu mediul, deoarece, în majoritatea cazurilor, timpul de reacţie se reduce substanţial de la ore la minute, randamentele sunt semnificativ mai bune, cantitatea în produși secundari este diminuată, iar unele sinteze au loc în absența solventului. În zilele noastre, iradierea cu microunde este aplicată cu succes în aproape toate tipurile de reacţii chimice, cu rezultate îmbucurătoare.
Cuvinte cheie: iradiere cu microunde, alternativă modernă și eficientă, prietenoasă cu mediul.

INTRODUCTION

Since the ’70s, microwave technology has been introduced to the field of chemistry, initially in inorganic chemistry. In the ’80s, the application of microwaves extended into organic chemistry, although at first there was some restraint, caused by limited understanding of microwave heating mechanisms. The situation changed significantly in the mid ’90s, when the number of publications in this field increased considerably [Bose *et. al.,* 1994]. Important contributions were made by Mingos and his collaborators [Gabriel *et.al.,* 1998], who explained the

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theoretical foundations of microwave heating, Gedye and Langa, which highlighted the specific effects of microwaves [Gegye and Wei, 1989; Langa *et. al.,* 1997], Loupy and his team [Loupy *et. al.,* 1998], which published numerous papers on „reactions without solvent”, as well as Strauss, which analyzed organic syntheses in high-temperature aqueous systems [Strauss, 1999].

Currently, the use of microwaves in chemistry has evolved significantly, becoming a technique established in organic and inorganic synthesis. Microwave ovens dedicated to the laboratory are equipped with temperature and pressure control systems, which allows reactions to high temperatures and pressures under safe conditions. This technology is considered a pillar of modern chemistry, being integrated into standard protocols and advanced research.

MATERIAL AND METHOD

Microwave heating gives the opportunity to quickly explore the chemical space [Edwards *et. al*., 2006]. It is successfully applied in almost all types of reactions, achieving more than gratifying results. The number of publications in the field is impressive, starting from alkylation reactions, acylation, saponification, transesterification, aminars, decarboxylation and disalkylation, elimination and nucleophilic aromatic substitution reactions, oxidation reactions, aldolic condensation reactions, Knovenagel condensation or eugenol isomerisation. Also, peptide synthesis, pyridazone, different metal catalysed reactions were performed. [Perreux and Loupy, 2001; Kappe, 2004].

Table 1

The main features of the reactions made by classical heating versus microwave irradiation

Classical heating	Microwave irradiation
▪ The reaction time varies from tens of hours to several days, which involves a lot of energy consumed	▪ The reaction time is significantly reduced (a few minutes), which prevents the decomposition, of reactants and products, as well as the occurrence of secondary reactions.
▪ Reactions are carried out at high temperatures, which can favour the occurrence of secondary reactions and degradation of products.	▪ The temperature increases evenly, reducing the risk of secondary product formation or product degradation.
▪ Heating is carried out indirectly by heat transfer (oil or sand baths), which generates temperature gradients, which can cause local overheating and decomposition of compounds. ▪ Thermal energy is introduced into the system through the walls of the pot, which limits the uniformity of heating.	▪ Electromagnetic energy is directly converted into heat by treated materials (liquids or solids), eliminating the need for an external heating environment. ▪ Dielectric heating allows electromagnetic radiation to cross the walls of the vessel and directly heat the reactants and solvent.
▪ Catalysts are needed to speed up the process, and the products obtained are often stable compounds, totally or partially.	▪ With this method, superior control over the reaction parameters is achieved, which favors higher yields and increased selectivity.

Table 1 highlights the main features of the reactions made by classical heating versus microwave irradiation, clearly emphasizing the undeniable advantages of this modern technology.

According to the data from the table, microwave heating is a modern and efficient alternative to classical methods, offering advantages such as reducing reaction time, uniformity of temperature and eliminating local overheating. This technology contributes to the development of green chemistry by reducing energy consumption and solvent use, being increasingly integrated into organic, inorganic synthesis and pharmaceutical industry.

The absorption and transmission of energy using microwave irradiation is completely different from conventional heating. Using microwaves, we use electromagnetic radiation (with the frequency located in the area 0.3 - 300 GHz). Electromagnetic radiation has two components: electric field and magnetic field, the first being responsible for the effect of microwaves on substances [Fini and Breccia, 1999].

RESULTS AND DISCUSSIONS

There are two mechanisms that explain the action of microwaves: *the dipolar polarization* and *ion conduction mechanism* - heating can be achieved by a single mechanism or a combination of the two [Kappe, 2004; Lidström *et. al,* 2001; Slocombe and Porch, 2021].

1. *Dipolar polarization mechanism* - occurs at polar molecules, because the dipole is sensitive to external electric fields and will align by rotation with the field. The amplitude of microwaves increases from zero in one direction, reaches a maximum, decreases to zero, and then increases and reaches a maximum in the opposite direction. The molecules on which the radiation acts respond by "polar rotation" (rotation of polar heads in the direction of amplitude). Following rotation, the molecules rub against each other instantly and evenly generating heat throughout the field. The time the change takes place is the same as the reaction time (response time).

In the case of gases, the molecules are far apart and their alignment with the applied field is rapid. However, the molecules no longer touch as they rotate, due to the large distance between them, so no phase difference will be generated.

Very important is the frequency applied for chemical synthesis:

- at low irradiation frequency (below 0.3 GHz) the molecules rotate, but they gain little energy, and the heating effect is small.

- at high frequencies of the electric field (over 300 GHz), the dipoles do not have enough time to respond to field oscillation, do not rotate, so no heating occurs.

- if the applied field is in the microwave radiation region (0.3 - 300 GHz), the molecules (dipoles) absorb energy from the applied electromagnetic field, rotate continuously, there are frictions and collisions, which will generate heat.

For example, if two samples, water and dioxane are heated in a microwave cavity, the final temperature will be higher in the water sample (Lidström *et. al,* 2001). Dioxane does not have a dipole moment and as such does not heat up, while the water with high dipole moment heats up immediately. So, the higher the dipole moment of a compound, the higher the tendency to absorb microwave radiation.

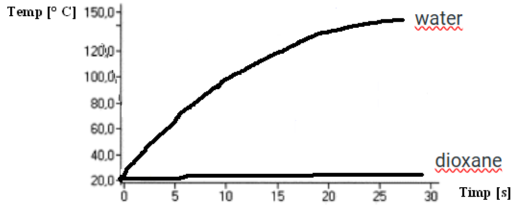

Fig. 1: Microwave action, at 150 W, for water and dioxane.

For this reason, non-polar solvents do not absorb microwaves and are not generally used in microwave assisted synthesis. The most used solvents are dimethylformamide, water, 2-butanone and methanol.

2. *The ion conduction mechanism* is stronger than the dipole polarization mechanism. The mechanism occurs in ion-containing solutions because the microwave electric field attracts free ions. There is an increase in the rate of collision of molecules, which leads to an increase in the amount of energy released into the solution (conversion of kinetic energy into heat).

In the case of two samples, with distilled water and drinking water, heated at the same time, in a microwave cavity, at a fixed power and for a determined time, the final temperature will be higher in the tap water sample (Lidström *et. al,* 2001), because the heat generated by the conduction mechanism, due to the presence of ions, is added the heat produced by dipolar mechanism.

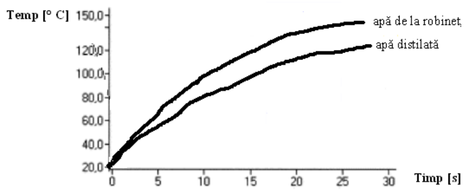

Fig. 2: Microwave action, at 150W, for distilled water and drinking water

The choice of solvent for liquid phase reactions in the microwave field is very important because the solvent must dissolve the reactants/products and absorb microwave radiation [Majetich and Hicks, 1994]:

- in polar solvents, with low molecular weight and high dielectric constant (water, alcohol), molecular dipoles quickly reorient under the action of microwaves, generate friction and convert electromagnetic energy into heat, in a very short time.

- non-polar solvents (hydrocarbons) do not absorb microwaves, but can be heated indirectly in microwaves, adding small amounts of polar solvent or solvent soluble salts.

For two solvents, with comparable dielectric constants, acetone and ethanol, heated to the same power and time, the final temperature will be much higher for ethanol than for acetone ($\varepsilon_{acetone} = 20.6$ and $\varepsilon_{ethanol} = 24.6$).

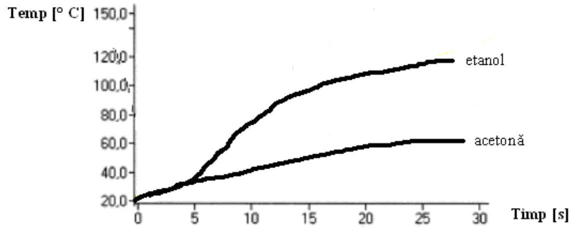

Fig. 3: Microwaves action, at 150 W, for ethanol and acetone.

Also, ion-containing solutions interact very quickly and powerfully with the microwave electric field. There is an increase in temperature, and the speed of reaction is further accelerated [Welton, 1999; Seddon, 1997].

Green chemistry aims to reduce pollution on the environment, especially avoiding more volatile solvents [Blass, 2002]. Thus, many reactions can be carried out under the action of microwaves in the absence of solvent. In this case, the recovery and purification of the solvent is no longer necessary, the effect of microwaves is more pronounced because the electromagnetic radiation is directly absorbed by the reactants, and the product can be obtained directly from the reaction mixture by distillation, extraction, sublimation. In the absence of the solvent, the reactions take place in solid phase (on recyclable and cheap mineral support: KF/Al2O3) or using transfer catalysis (modern and efficient method of making contact between two immiscible phases; the transfer of the reagent into the organic environment is carried out by transfer catalysts - KF/Aliquat 336 or K2CO3/Aliquat 336, and the reaction takes place only in the organic phase).

CONCLUSIONS

Microwave irradiation generates heat to substances with dipole moment (dipole is sensitive to external electric fields, will try to align by rotation with the field and by this rotation produces energy). The mechanism also occurs in solutions containing ions (the microwave electric field attracts free ions, increases the rate of collision of molecules, which leads to the conversion of kinetic energy into heat).

Microwaves are currently used to: accelerate chemical reactions (reducing reaction time from hours to minutes), increase in yield and selectivity (obtaining desired products with fewer secondary products), green techniques (reactions without solvent or with reduced amounts of solvents, contributing to sustainable chemistry), synthesis of advanced materials (nanoparticles, catalysts, specialized polymers), and pharmaceutical industry (for rapid synthesis of bioactive compounds) and analytical chemistry (sample digestion and rapid extraction of compounds).

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