

Online Class of Chemistry Honours Sem – VI , DSE - 3

BY

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Use of Micro Wave and Ultrasonic Energy in Green Process

1. Microwave induced green synthesis With increasing community concern over possible influences of chemicals and chemical practices on the environment microwave induced green synthesis has received considerable attention for direct, efficient, and environmentally unobtrusive synthesis. By using this technique , considerably shorter reaction times than normal had been obtained for common organic transformations such as esterification, hydrolysis, etherification, addition, and rearrangement. Inadequate controls in the rudimentary equipment employed, however, generated hazards, including explosions. In the electromagnetic radiation spectrum, microwaves (0.3 GHz–300 GHz) lie between radiowave (Rf) and infrared (IR) frequencies with relatively large wavelength. Microwaves, a non-ionizing radiation incapable of breaking bonds, are a form of energy and not heat and are manifested as heat through their interaction with the medium or materials wherein they can be reflected (metals), transmitted (good insulators that will not heat) or absorbed (decreasing the available microwave energy and rapidly heating the sample).Microwave reactions involve selective absorption of electromagnetic waves by polar molecules, non-polar molecules being inert to microwaves. When molecules with a permanent dipole are submitted to an electric field, they become aligned and as the field oscillates their orientation changes, this rapid reorientation produces intense internal heating. The main difference **between classical heating and microwave heating lies in core and homogenous heating associated with microwaves, whereas classical heating is all about heat transfer by preheated molecules. In microwave induced organic reactions, the reactions can be carried out in a solvent medium or on a solid support in which no solvent is used** .For reactions in a solvent medium, the choice of the solvent is very important. Microwave chemistry generally relies on the ability of the reaction mixture to efficiently absorb microwave energy, taking advantage

of “microwave dielectric heating” phenomena such as dipolar polarization or ionic conduction mechanisms. In most cases this means that the solvent used for a particular transformation must be

- 2. Microwave absorbing.** The ability of a specific solvent to convert microwave energy into heat at a given frequency and temperature is determined by the so-called loss tangent ($\tan \delta$), expressed as the quotient, $\tan \delta = \epsilon''/\epsilon'$, where ϵ'' is the dielectric loss, indicative of the efficiency with which electromagnetic radiation is converted into heat, and ϵ' is the dielectric constant, describing the ability of molecules to be polarized by the electric field. A reaction medium with a high $\tan \delta$ at the standard operating frequency of a microwave synthesis reactor (2.45 GHz) is required for good absorption and, consequently, efficient heating. Microwave ovens offer a clean and sometimes cheaper alternative to oil baths for many organic reactions. Microwave synthesis can be performed either under sealed-vessel or open-vessel conditions. Reactions performed in sealed vessels can reach temperatures much higher than the boiling point of the solvent used at elevated pressure. In open-vessel microwave assisted reactions, reactions are carried out at atmospheric pressure; yet solvents can still reach temperatures that are 10–20°C above their boiling points,^{91–94} which may be explained by the occurrence of instantaneous hot spots. An excellent solvent in a domestic microwave oven is N,N-dimethylformamide (DMF) (b.p. 160°C). Open-vessel synthesis allows for any gases that may be generated in a reaction to evolve from the reaction environment possibly causing reactions to progress further to completion than when performed in a sealed vessel. Also, open-vessel reactions can be performed using standard laboratory glassware, such as round-bottom flasks and reflux condensers, in the microwave cavity allowing reactions to be carried out on a larger scale. Since microwave synthesis was introduced in the literature, there has been an explosion of applications to organic synthesis, inorganic synthesis, and organometallic synthesis. Loupy has described a solvent free/microwave method for the synthesis of aromatic ethers by the S_NAr reaction of 4-nitro-substituted halogenobenzenes or 2-halonaphthylenes, but only phenol was employed. Similar results have been achieved by Bogdal, who prepared a range of aromatic ethers by reaction of phenols with primary alkyl halides under microwave heating, however, in the presence of TBAB. Also Fan has employed the same strategy for the reaction of 1-chloro-4-

nitrobenzene and phenolates, affording 4-nitrodiphenyl ethers. Liet al. reported the microwave-assisted coupling of phenols, including those having a strong electron-withdrawing group, with aryl halides in the presence of potassium carbonate providing diverse diaryl ethers with high to excellent yields.

Green Solvents

3. Organic Solvents : Ionic Liquids : In Organic Synthesis Ionic liquids are mixtures of anions and cations, molten salts, with melting point around 100°C, which can be used as alternative solvents in organic synthesis. Although the ionic liquids do not completely full with green chemistry principles, they are very promising as alternatives to organic solvent.

Supercritical carbon dioxide and supercritical water : A supercritical liquid is at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist. The supercritical liquid can effuse through solids like a gas, and dissolve materials like a liquid. In addition, close to the critical point, small changes in pressure or temperature result in large changes in density, allowing many properties of a supercritical fluid to be "fine-tuned". Supercritical liquids are suitable as a substitute for organic solvents in a range of industrial and laboratory processes. Carbon dioxide and water are the most commonly used supercritical fluids. Supercritical CO₂ and water are considered "green" solvents in many industrial processes, providing high yields in many reactions, and there are many examples of their use in the scientific literature.

Organic Synthesis in Water Although water is considered a problem for organic synthesis and the purification processes and drying in final products is very cumbersome, in recent years water is considered a good solvent for organic reactions. A good example is the synthetic routes of the Diels-Alder reactions in which the hydrophobic properties of some reagents makes water an ideal solvent. Water as a solvent accelerates some reactions because some reagents are not soluble and provides selectivity. The low solubility of Oxygen is also an advantage for some reactions where metal catalysts are used. In the last

years water is used in many methods for organic reactions and the scientific literature has a large number of papers.

Fluorous Biphasic Solvents : Fluorinated compounds with appropriate melting and boiling points can be used as solvents. The character of fluorinated solvents is dependent on the percentage of fluorine contained in these compounds. Highly fluorinated solvents such as perfluorohexanes are often immiscible with common organic solvents, and form a fluorous phase. These solvents are termed pure fluorous. On the other hand, less fluorinated solvents like benzotrifluoride (BTF) are miscible with organic solvents as well as pure fluorous solvents. These solvents, called hybrid or amphiphilic solvents, act in the same manner as common organic solvents; however their fluorous character remains and often shows itself during organic reactions by promoting reactivity or selectivity of the processes. This chapter focuses on how pure fluorous and hybrid solvents are utilized in organic reactions.

Here the analysis of alternative solvent systems as “greener” replacement for traditional organic solvents has been focused on ionic liquids, fluorous solvents and supercritical fluids, described below, mainly by taking into account their applicability as reaction media in biocatalysis.

Fluorous solvents Properties and applications : ‘Fluorous’ was the term coined for highly fluorinated (or perfluorinated) solvents by Horvath, in an analogous way to “aqueous” for water-based systems. Perfluorinated compounds (PFCs) have been produced since the 1950s and used for many industrial applications as cosmetics, fire fighting foams, food packaging, water and grease repellents, coatings for fabrics. This widespread use is due to PFCs unique physical-chemical properties, and in particular to a better effectiveness and a higher chemical and thermal stability than non-fluorinated chemicals, correlated to the strength, the chemical inertness and the low polarizability of C-F bonds. Nowadays fluorine chemistry has also an important role in clean technology, both in catalysis and in solvents replacement fields. Several applications in organic chemistry involve perfluoroalkanes like FC-72 (a mixture of perfluorohexanes) or PFMC (perfluoromethylcyclohexane), which are extraordinarily non-polar and form biphasic mixtures with many organic solvents or with water. However fluorous solvents commonly exhibit temperature-dependent miscibility (thermomorphism) with organic

solvents and it means that they can be used in fluoruous/organic biphasic systems (FBS) in which catalysts, with high affinity for fluoruous solvents, and organic reagents, soluble in the organic solvents, can react in one-phase at higher temperature and separated in a biphasic system at lower temperature. In this sense fluoruous solvents can be considered as switchable, as the switchable polarity solvents.

The peculiar feature has led to the development of fluoruous biphasic chemistry, in which the efficiency and the recycling of the system are improved by a better and easier separation of products from catalysts.

Polyethylene glycol (PEG) :

The application of polyethylene glycol (PEG) aqueous solution as a green solvent in microwave-assisted extraction (MAE) was firstly developed for the extraction of flavone and coumarin compounds from medicinal plants. The PEG solutions were optimized by a mono-factor test, and the other conditions of MAE including the size of sample, liquid/solid ratio, extraction temperature and extraction time were optimized by means of an orthogonal desig. Subsequently, PEG-MAE, organic solvent-MAE, and conventional heating reflux extraction (HRE) were evaluated with nevadensin extraction from *Lysionotus pauciflorus*, aesculin and aesculetin extraction from *Cortex fraxini*. Furthermore, the mechanism of PEG-MAE was investigated, including microwave-absorptive property and viscosity of PEG solutions, the kinetic mechanism of PEG-MAE and different microstructures of those samples before and after extraction. Under optimized conditions, the extraction yields of nevadensin from *L. pauciflorus*, aesculin and aesculetin from *C. fraxini* were 98.7%, 97.7% and 95.9% in a one-step extraction, respectively. The recoveries of nevadensin, aesculin and aesculetin were in the range of 92.0-103% with relative standard derivation lower than 3.6% by the proposed procedure. Compared with organic solvent-MAE and conventional extraction procedures, the proposed methods were effective and alternative for the extraction of flavone and coumarin compounds from medicinal plants. On the basis of the results, PEG solution as a green solvent in the MAE of active compounds from medicinal plants showed a great promising prospect.

