Microwave chemistry

CHEMICAL SOCIETY REVIEWS

Saskia A. Galema

Unilever Research Laboratory, Olivier van Noortlaan 130, 3130 AT Vlaardingen, The Netherlands

In this article the application of microwave dielectric heating in chemistry is reviewed. The principle of microwave dielectric heating is described and relevant instrumentation is described briefly. The effects observed following microwave heating are discussed. Specific attention is given to chemical reactions which have been carried out advantageously in a microwave oven.

1 Introduction: dielectric heating and instrumentation

Microwaves are electromagnetic waves. Electromagnetic waves contain electric and magnetic field components. The electric field applies a force on charged particles as a result of which the charged particles start to migrate or rotate. Due to the movement of charged particles further polarisation of polar particles takes place. The concerted forces applied by the electric and magnetic components of microwaves are rapidly changing in direction (2.4×10^9 per second) causing warming because the assembly of molecules, *e.g.*, a liquid or a semi-solid, cannot respond instantaneously to the changing direction of the field and this creates friction which manifests itself as heat.

The frequencies allotted for microwave dielectric heating (also referred to as microwave heating or dielectric heating) are 918 MHz and 2.45 GHz, with the latter frequency being used most often. The latter is also applied in domestic microwave ovens. These frequencies correspond to respective wavelengths of 33.3 and 12.2 cm which are in the region between the infrared and radiowave wavelengths in the electromagnetic spectrum.

The properties ε' and ε'' are associated with the extent of heating which the material can undergo in a dielectric field. The exact dependence of the heating rate upon the presence of a dielectric field is given by eqn. (1).

$$\tan\delta = \varepsilon'/\varepsilon'' \qquad (1)$$

ε' is the relative permittivity, which is a measure of the ability of a molecule (or assembly of molecules) to be polarised by an electric field.

ε'' is the dielectric loss, which is indicative of the ability of a medium to convert dielectric energy into heat.

$\tan\delta$ is the dielectric loss tangent and defines the ability of a material to convert electromagnetic energy into heat energy at a given frequency and temperature.

The value of $\tan\delta$ of an assembly of molecules depends on several factors: on the frequency of the electromagnetic waves, the temperature and the physical state and composition of the mixture.

For water, the relative permittivity ε' decreases when the microwave frequency increases, but the dielectric loss factor ε'' increases in the frequency range of 3×10^8 to 1×10^{10} Hz. The presence of electrolyte (*e.g.* NaCl)[1] does not seem to influence the relative permittivity significantly, but has a marked effect on the dielectric loss factor, specifically at frequencies of 3×10^8 and 3×10^9 Hz.[1]

Dielectric heating rates depend on the value of $\tan\delta$, but also on the size/quantity of the reaction mixture and (as for conventional heating) on the heat capacity of the medium. The consequence of an increasing volume of the reaction mixture is that incident microwaves suffer an absorbance loss factor and the depth of penetration of the incident radiation is related to $\tan\delta$. The penetration depth is given by eqn. (2).

$$D_{\mathrm{p}} = \lambda_{\mathrm{o}}\sqrt{(\varepsilon'/\varepsilon'')} \qquad (2)$$

In this equation, D_{p} is the penetration depth, λ_{o} is the wavelength of the microwave radiation.

Instrumentation which has been used in microwave applications is quite varied and has been described and discussed in the microwave chemistry reviews quoted below. Specific literature can also be found in the following two journals: the '*Journal of Microwave Power and Electromagnetic Energy*' and '*Microwave World*'.

Microwave ovens can range from simple household multimode ovens to large scale batch as well as continuous multimode ovens. In some cases glassware has been redesigned in order to be able to carry out reactions in multimode microwave ovens. In other cases, batch closed reactor vessels or turntables able to contain a number of reaction vessels have been applied. Specifically, in the food industry large-scale (continuous mode) ovens are used frequently. For specific research purposes single mode microwave ovens with options for batch or continuous processing have been designed. In addition, it has not been uncommon to design ovens for individual purposes.

2 Microwave chemistry

2.1 Introduction

Considerable knowledge of microwave radiation was obtained during the development of radar before and during the second world war. In the late 1960s it was used as a heating mode for

Saskia A. Galema received her MSc degree in 1988 from the University of Groningen, The Netherlands, after carrying out kinetic studies on the effect of cosolvents on selected organic and inorganic reactions in aqueous solutions at both the University of Groningen (J. B. F. N. Engberts) and the University of Leicester, UK (M. J. Blandamer and J. Burgess). Subsequently, a study of the effect of stereochemistry of carbohydrates on their hydration led to a PhD at the University of Groningen in 1992 (J. B. F. N. Engberts). During this period she also carried out collaborative research in Bergen, Norway (H. Høiland) and at the NIKO-TNO in Groningen (H.A. van Doren). Since the beginning of 1993, she has been working as a research manager at the Unilever Research Laboratory in Vlaardingen, The Netherlands. Initially she worked in the Organic Chemistry Unit studying microwave chemistry, but since mid-1995 she has been project manager for flavour encapsulation in the Exploratory Research Foods Group.

temperature-jump experiments.[2] The first application in chemical research was reported in the early 1970s, when gas-phase discharge was applied to realise decomposition of simple organic compounds.[3] By the early 1980s, two patents had appeared concerning polymer chemistry and one concerning starch derivatisation.

However, when significant rate accelerations for reactions carried out in a conventional microwave oven[4,5] were observed in 1986, this led to considerable increased attention on reactions carried out while subject to dielectric heating. In addition, more advanced microwave ovens were designed. Moreover, discussions on the causes of microwave reaction rate enhancements, apprehensions about temperature monitoring, and control and trials of large-scale reactions in microwave ovens, ensued.

The subject of microwave chemistry has been extensively reviewed. Microwave chemistry was the subject of the 1991 Tilden lecture published in this journal.[1] Since then further reviews have been published by Gedye,[4] Abramovitch,[6] Mingos,[7] Berlan[8] and Majetich[5] and coauthors. The reviews of Gedye, Majetich and Abramovitch are more focused on the type of reactions which have been carried out in microwave ovens, with emphasis on organic reactions. Specifically Gedye and Majetich have reviewed their own extensive studies. Abramovitch provides some additional information on how microwave heating can be used in analytical and food chemistry. Berlan has covered industrial applications as well.

Organic reactions such as esterification, etherification, hydrolysis, substitution reactions and Diels–Alder reactions have been studied comprehensively in the microwave oven and relevant examples can be found in the reviews discussed above.

In addition, there is a relatively abundant literature on this subject; articles are often published in journals such as *Tetrahedron Letters* and *Synthetic Communications*.

Microwave heating has not been restricted to organic chemistry as various aspects of inorganic chemistry[1] and polymer chemistry (specifically polymer curing) have also been investigated. One might be led to believe that there really is a different type of chemistry discussed by Bose *et al.* when they introduced the term MORE (microwave-induced organic reaction enhancement) chemistry.[9] However, usually the same chemistry (*cf.* 'conventional' heating) has been observed when the organic reactions involved were carried out. The difference lies in the choice of reaction conditions: the reactions were carried out in high boiling solvents with a significant tanδ (*e.g.* DMF). Heating is fast, but maximum temperatures were chosen below the boiling point of the solvent in order to avoid solvent evaporation. Thus one could work in open reaction vessels, could chose small amount of solvent when targeting for solubility at the reaction temperature. Overall Bose claims that the method is more cost-effective (only simple glassware needed) and environmentally friendly (less solvent needed).

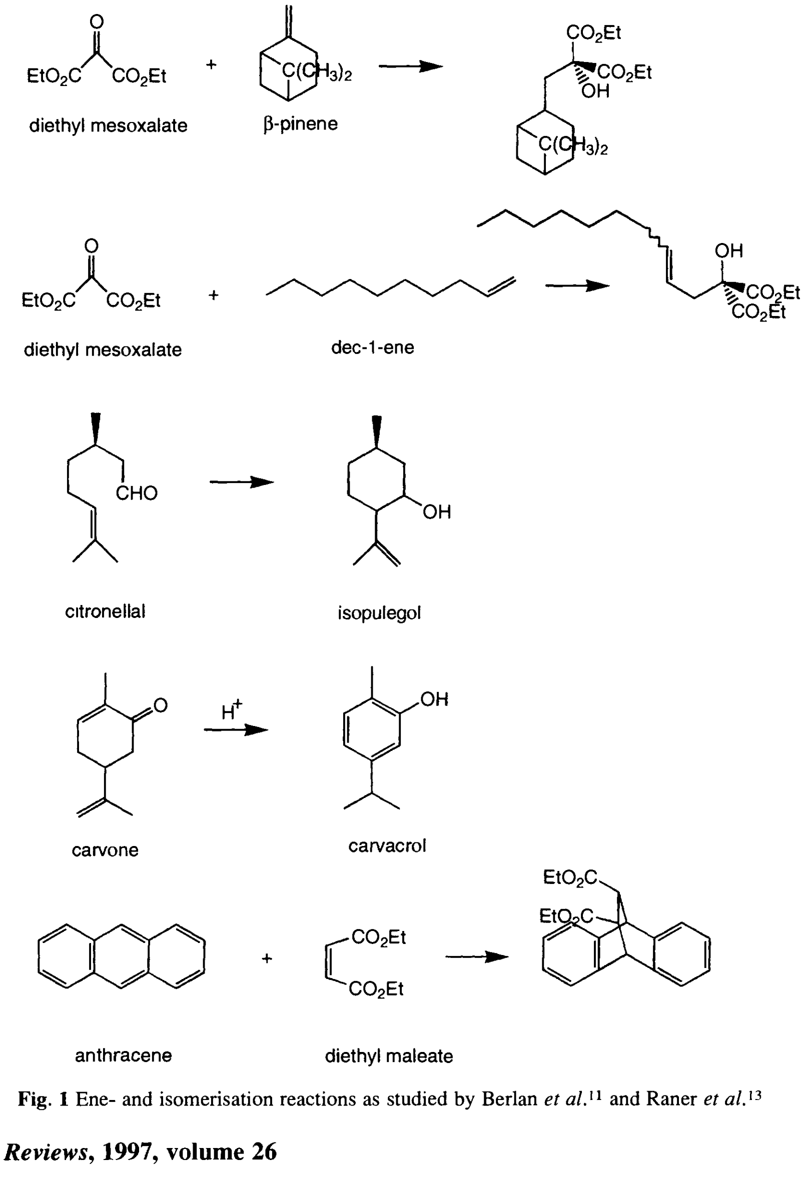

Fig. 1 Ene- and isomerisation reactions as studied by Berlan *et al.*[11] and Raner *et al.*[13]

The effect of microwave heating on enzymes has been studied but no specific effects have been observed.[10]

2.2 Claimed effects of microwave dielectric heating

Claimed effects of microwave dielectric heating can be divided into two kinds: thermal effects and non-thermal effects. Thermal effects are those which are caused by the different temperature regime which can be created due to microwave dielectric heating. Non-thermal effects are effects which are caused by effects specifically inherent to the microwaves and are not caused by different temperature regimes.

2.2.1 Temperature effects

Mingos has described which effects can be expected when reactions are being carried out in a microwave dielectric field. He describes the factors which play a role in microwave heating: (1) superheating in the presence of a large number of ions; (2) more rapid achievement of the reaction temperature and (3) efficient mixing and boundary effects.

These effects have been observed and have also been described as rapid heating effects, hot spots or surface effects and pressure cooker effects.

2.2.1.1 Effects of rapid heating

In the case of preparation of intercalation compounds a better crystallinity can be obtained, and in the case of zeolite and ceramic processes there is also an advantage to be gained. The rate acceleration effect is increased if microwave energy is absorbed by the reactants themselves and not by an absorbent, for example by the solvent.

In the case of polymer curing the rapid heating is also thought by most researchers to be the cause of the better curing yields.

2.2.1.2 Hot spots, surface effects

Specifically in the case of solids being heated in the microwave oven, there are some dramatic effects with respect to heating rates,[1] whereas in organic solvents there is not really any thermal effect. The synthesis of many organometallic compounds under microwave radiation reflux conditions is accompanied by a decrease in reaction time. These effects can be exploited in the efficient synthesis of complexes of second and third row transition metal ions which are considered difficult to prepare under standard conditions, but can be readily produced in a microwave oven.

Problems with field and energy distribution have been identified,[8] but then again these can also be used as an advantage: local 'hot-spots' can be used to synthesise germanium derivatives.

2.2.1.3 Pressure cooker effect

The reaction media used in the experiments of Gedye and Majetich were generally heated to quite high temperatures and (sometimes) also high pressures. The high temperatures could have been the cause of the rate accelerations observed. In some cases it was claimed that the temperature effects observed during microwave heating could be caused by local 'hot spots' which would occur while the bulk temperature remained low. When conventionally heated reactions were carried out in a sealed tube the yield of reaction became comparable to those carried out in the microwave oven (studied for Diels–Alder reactions in DMF). This finding illustrates that the temperature effect due to the build up of pressure in the sealed tubes accounts for the effects observed during microwave heating.

2.2.2 Non-thermal microwave effects

Non-thermal microwave effects come to mind when one thinks of microwave spectroscopy. However, microwave dielectric heating is specifically different from microwave spectroscopy, which is carried out in the gas phase and for which discrete energy levels of excitation can be observed. This is in contrast to dielectric heating during which no molecules can be excited into higher energy levels. Therefore, microwave dielectric heating should not be confused with microwave spectroscopy.

Non-thermal effects were claimed initially by Gedye *et al.*[4] and Majetich *et al.*[5] when they observed significant rate enhancements for hydrolysis and esterification reactions. However, reevaluation of reaction rates under conventional conditions revealed that sometimes reaction times suggested in the literature were erroneously long.

Although there was a general agreement that microwaves contain only 1 J per mole of photons, there were still claims of special effects[11] such as lowering of Gibbs energy of activation of reactions. This was envisaged to happen through either (1) storage of microwave energy in the vibrational energy of a molecule by *e.g.* an antenna group (enthalpy effect) or (2) by alignment of molecules (entropy effect).

The discussion which involved this issue is interesting. Of course it would be quite exciting if it had been established that there is a non-thermal microwave effect. This could have far reaching consequences for reaction chemistry. In the food industry it would be of great concern if there could be reactions taking place during microwave heating which would not take place during conventional cooking or were not thought viable by normal thermal conditions.

Finot and Merabet[12] have reviewed thoroughly the work carried out in food research and came to the conclusion that no non-thermal microwave effects have been observed when food was dielectrically heated. They observed that any effect observed during microwave heating could be reproduced when food mixtures were heated under conventional conditions.

In the field of reaction chemistry, however, initially it was believed that there was a non-thermal microwave effect when Diels–Alder reactions were carried out under homogeneous reaction conditions (both in apolar as well as slightly polar reaction mixtures)[11] since reaction halflives seemed to depend on the heating mode, despite comparable bulk temperatures.

However, when careful temperature control was guaranteed, no special rate effects were observed. This was confirmed for ene reactions[11] as well as for isomerisation reactions and Diels–Alder reactions.[13] Neither of the researchers found a reproducible microwave effect. Ref. 13 provided the first example of a systematic study to determine and evaluate activation parameters for reactions both heated dielectrically and conventionally. No differences depending on heating mode were observed. Reactions studied were the isomerisation of carvone and the Diels–Alder reaction between diethyl maleate and anthracene, and the acid catalysed esterification of 2,4,6-trimethylbenzoic acid in isopropyl alcohol. It was also argued by Raner *et al.*[13] that the notion that microwaves can excite rotational or vibrational transitions is invalid. A specific adjustment of the microwave oven was needed to guarantee a constant temperature during microwave heating with a constant presence of a dielectric field.

Thus, it was concluded that most rate enhancement effects were observed during microwave heating because there was inadequate temperature monitoring and control.

However, this did not signal the end of the debate and apparent observation of a 'special effect' when dielectric heating was used. Within the field of polymer chemistry there has been no clarity regarding whether effects observed were non-thermal or not. Yet, for the epoxy-amine kinetics of curing of a polymer under careful temperature conditions no effect was observed.[14]

However, a faster curing and cross-linking in the initial stages of the reaction of epoxyresin has been observed upon dielectric heating and it was claimed that this is caused by the fact that part of the reactants are trapped.[15] It has been postulated,[16] that the secondary amine groups have become more reactive. The differences between microwave cured and thermally cured polymer have been rationalised in terms of the temperature profile during the initial stages of the reaction or specific activation. This will be the cause of the occurrence of cross-linking reactions earlier in the reaction stage. A study of the intramolecular imidisation reaction between BTDA† and DDS polyamic acid in *N*-methylpyrrolidone and cyclohexylpyrrolidone under different heating condition gave rise to the observation that the rates of this reaction were determined by the heating mode.[16] The reaction was followed by IR spectroscopy. This effect was thought to be caused by temperature 'hot-spots' at a molecular level which could be up to 50 °C higher than the bulk temperature.

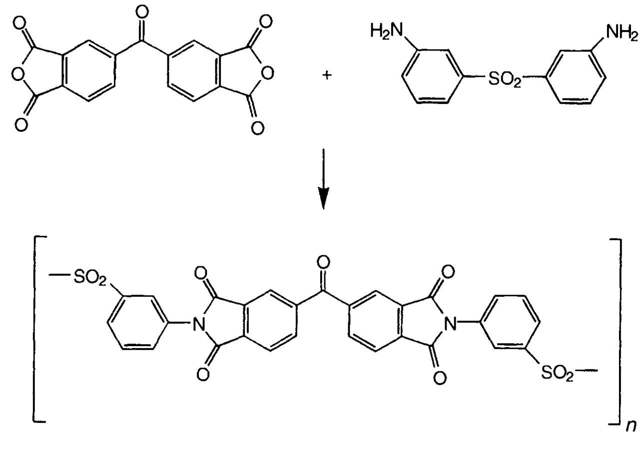

Fig. 2 The intramolecular imidisation reaction between BTDA and DDS

When proper control was maintained the different temperature regimes which can be realised in a microwave oven could be employed to control the isomeric ratios of the products of the sulfonation of naphthalene.[17] This seems a route to make either the kinetically or the thermodynamically controlled reaction product.

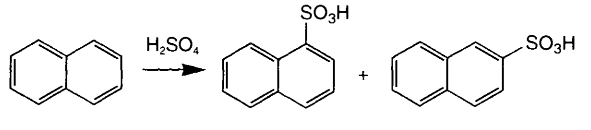

Fig. 3 The sulfonation of naphthalene leading to a kinetically and thermodynamically controlled reaction product

For the mutarotation of glucose specific effects on the ratio of α- to β-glucose produced were observed when microwave heating was applied.[18] This specific effect was apparent in ethanol–water mixtures.

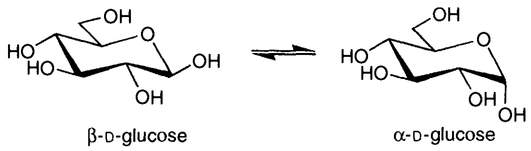

Fig. 4 The mutarotation of glucose

2.3 Temperature monitoring and control

Reliable temperature control and measurement present a significant technical challenge when employing dielectric heating. Thus, once it was realised that temperatures effects or superheating[7,19] might account for a significant part of the observed effects, considerable effort was devoted to temperature monitoring in the microwave oven. As no metals could be used in the microwave oven, alternative methods were sought. Some examples of thermometers which have been applied are gas thermometers,[19] shielded thermocouples,[20] thermocouples which are claimed not to be self heating,[21] IR thermal imaging,[22] thermochromic dyes or thermochromic liquid crystals[16] and fluoroptic monitoring (luxtron thermometers).[17]

Temperature control has proven very difficult, especially when reactions are being carried out in closed reaction vessels. Given that most standard microwave ovens can only supply power in a pulsed mode, there are five possibilities for control of the temperature: (1) control of power input; (2) dilution of power input;[9,18] (3) allowing the reaction mixture to be at reflux conditions; (4) by setting a pressure limit (in closed vessels supplied with a pressure release system, the maximum temperature can be set *via* the setting of the pressure);[7,23] (5) allow for adequate mixing in the reaction vessel in conjunction with control of power input.[24]

Modelling of the electromagnetic field strength has been attempted as well in order to have a better understanding of the temperature distribution.[8]

In addition, the use of flow systems in the microwave oven can assist in achieving a level of temperature control.[7,25]

2.4 Some examples of advantageous use of dielectric heating

There are many examples of different types of chemistry practised while applying a dielectric field. In this section I would like to focus on areas within chemistry in which a clear advantage of the creation of a different temperature regime and its consequences have been shown.

2.4.1 The synthesis of radiopharmaceuticals

Radiopharmaceuticals are often used in medical research, and frequently need to be prepared quickly and immediately before their application, otherwise the compounds lose a significant amount of their needed radioactivity. In this context, radiochemical yields are at least as important as chemical yields and, therefore, time is a critical factor. The use of dielectric heating in conjunction with closed Teflon (microwave transparent) vessels offer an opportunity to reduce reaction times.

The applicability of microwave heating has been demonstrated for fluoroalkylations of secondary amines,[23] for which it was found that increase of the ionic strength of the reaction mixture is a favourable factor for increasing yields of reactions. A similar objective is accomplished by increasing the strength of the electromagnetic field.[26] Aromatic substitution reactions using radioactive fluoride have also been studied in a microwave oven.[1] For these reactions, influences of the geometry of the sample, the microwave intensity and the polarity of the medium were observed.

Recently, a radiochemical yield improvement for the synthesis of 2-[^{18}F]fluoro-2-deoxyglucose by application of dielectric heating has been reported.[27]

2.4.2 Silica preparation, synthesis of inorganic complexes and intercalation reactions

Another area in which the different temperature regimes are advantageous is in zeolite preparation.[28] Because of the temperature regime in the microwave oven some zeolites show faster crystalline growth than under conventional conditions, due to the rapid dissolution of the gel. This effect was observed for hydroxysodalite prepared with sodium or tetramethylammonium salts. In addition, sintering of oxide ceramics (Al_2O_3–MgO and Al_2O_3:ZrO_2–SiO_2 mixtures) in a single mode cylindrical cavity applicator resulted in composites with fine grain size and a high density.[29] Similarly, the applicability of dielectric heating for the synthesis of chalcopyrite from the pure elements has been shown.[30] Calcination of metal oxide (precursors) on activated carbon catalysts, which usually is carried out in a muffled furnace could be carried out by heating the reaction mixture for 10 min in a microwave oven at 2.45 GHz.[31] Specifically for Co_3O_4 on activated carbon the effect of dielectric heating was found to be advantageous.

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† BTDA = Benzophenone-3,3′,4,4′-tetracarboxylic acid dianhydride. DDS = Diaminodiphenylsulfone.

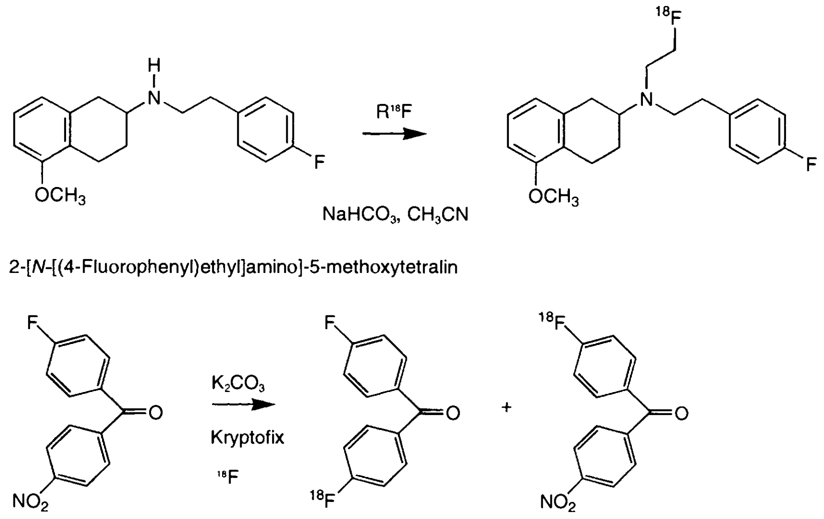

Fig. 5 Some reactions studied in the microwave oven which involve radio isotopes[23,26]

But the most dramatic and optimal use of microwave dielectric heating and its temperature effects has been recently shown by Mingos *et al.*[32] In their paper they describe the synthesis of a copper complex [Cu(pyhy)$_2$·2-melamine], a supramolecular complex which could only be synthesised by the use of the superheating effects induced by microwave heating. It appears that the starting materials have greatly increased solubility in the dielectrically heated medium and this facilitates reaction.

2.4.3 *Organic reactions under 'dry reaction conditions'*

Because dielectric heating is direct, and is effective when the matrix has a sufficiently large dielectric loss tangent, and contains molecules possessing a dipole moment, the use of a solvent is not mandatory for the conduction of heat. Therefore, the use of 'dry reaction mixtures' is an option in microwave chemistry, and has the advantage that solvent evaporation and/or unwanted pressure increases in a sealed tube are avoided under these circumstances.

These 'dry' reaction conditions have been employed for the phase transfer catalysed alkylation of carboxylic acids using Aliquat (a trade name for a tetralkylammonium salt) as a phase transfer catalyst. In addition, acid catalysed esterifications on various solid supports such as montmorillonite KSF, with or without isopropenyl acetate (a water scavenger), or the zeolite 13X, or with toluene-*p*-sulfonic acid as a catalyst, have been conducted. Moreover, transesterifications have been reported using various modified alumina carriers or montmorillonite, Spherosil or Amberlyst a.o.[33] The yields for these reactions are high (*ca.* 80%), and the rate of the reaction depends on the size of the batch. Temperatures measured at the end of the reaction time could rise to 140–200 °C. It is generally believed, especially for a reaction for which equilibrium could be shifted by evaporation of one of the products, the application of microwave heating under dry reaction conditions is a promising alternative.

The dry hydrolysis of nitriles can also be studied under these conditions without any carrier material.[8] No microwave kinetic effect has been observed, but at high temperatures microwave heating is claimed to give rise to improved yields and better selectivities.

The oxidation of dihydropyridines can be advantageously carried out in a microwave oven with bentonite as a carrier material.[34] However, not only is the oxidation taking place, but also dealkylation can occur depending on the character of the 4-alkyl substituent.

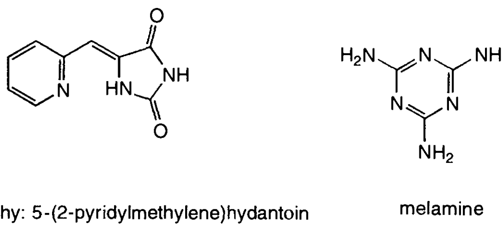

Fig. 6 The structure of Hpyhy and melamine

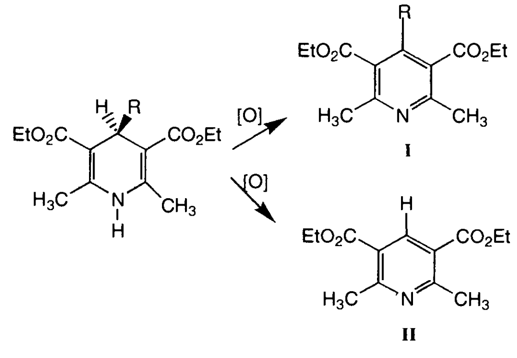

Fig. 7 The oxidative dealkylation of 4-alkyl-1,4-dihydropyridines with MnO_2 on bentonite

Table 1 Yield of normal pyridine and dealkylation products for different 4-alkyl substituted dihydropyridines after 10 min of irradiation time[34]

Substituent R	I, % yield	II, % yield
H	—	100
Me	54	23
Et	60	38
Pr	42	58
Pr^i	—	92
PhCH(CH$_3$)	—	84

2.4.4 *Plasma chemistry*

When a microwave discharge is incident on a gas phase system and a plasma is being formed, molecules can be synthesised from or react with gas phase molecules. This approach has been successfully applied by Wan *et al.*[35] for the decomposition of olefins over nickel powder and the decomposition of alkyl- and aryl-halides over metal containing catalytic surfaces (*e.g.* iron oxide on aluminium oxide).

2 4 5 *Analytical chemistry*

Analytical chemists have found many advantages to the use of microwave heating Sample preparations involving combustion or acid digestion, which used to be tedious experiments, have been transformed into rapid and manageable experiments, since the preparations are accelerated by using Teflon containers in a microwave oven In this domain of chemistry, clearly temperature effects are exploited optimally The extraction of volatiles, both important for environmental studies as well as for flavour studies has been carried out successfully using the microwave method [36] The approach has been called the MAP (microwave assisted process) approach Among others Kjeldahl distillations have been submitted to dielectric heating

2 4 6 *Polymer curing*

Because of the fast heating rates, polymer curing can be brought about quickly by applying dielectric heating, and the practice is widespread It is obvious that the faster heating rates which can be realised during microwave heating are an important factor Whether other effects also play a role has been discussed in section 2 2

3 Conclusion

Microwave chemistry has received considerable attention in the last decade, and its scope and limitations have essentially been established Although initially both thermal and non-thermal microwave dielectric heating effects have been claimed, it now seems to be generally accepted that a different temperature regime caused by microwave dielectric heating is the main contributing factor to any acceleration observed The thermal effect can be either caused by a faster initial heating rate or is due to the occurrence of local spots with higher temperatures In addition, it can be created by the use of 'pressure cookers'

Overall the subject has led to studies in three principal directions (1) Improved monitoring and control of temperatures, (2) The design of advanced (batch or continuous) microwave ovens, (3) Further exploitation of temperature effects

Investigation of the exploitation of temperature effects has led to successful applications in the area of the synthesis of radiopharmaceuticals, silica preparation, preparative inorganic chemistry, analytical chemistry, plasma chemistry and polymer curing Undoubtedly, further developments will occur and we can expect other important applications of microwave dielectric heating to be reported

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