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TILDEN LECTURE*

Applications of Microwave Dielectric Heating Effects to Synthetic Problems in Chemistry

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1 Introduction

Dr. Johnson's Dictionary of 1775 defined chemistry as 'an art whereby sensible bodies contained in vessels ... are so changed by means of certain instruments, and principally fire, that their several powers and virtues are thereby discovered, with a view to philosophy or medicine'. Although fire is rarely used these days the heating of chemicals in containment vessels still remains the primary means of stimulating chemical reactions which proceed slowly under ambient conditions. Since Johnson's time, however, photochemical, catalytic, sonic, and high pressure techniques[1] have been added to the chemist's repertoire for accelerating chemical reactions. In this review we describe an alternative to conventional conductive heating for introducing energy into reactions. The microwave dielectric heating effect uses the ability of some liquids and solids to transform electromagnetic energy into heat and thereby drive chemical reactions. This *in situ* mode of energy conversion has many attractions to the chemist, because its magnitude depends on the properties of the molecules. This allows some control of the material's properties and may lead to reaction selectivity. This application of microwaves should not be confused with gas phase reactions where a microwave discharge can create a plasma with a very high temperature and can cause dramatic fragmentation and recombination reactions.

A reliable device for generating fixed frequency microwaves was designed by Randall and Booth at the University of Birmingham as part of the development of RADAR during the Second World War. This device, the magnetron,[2] was produced in large numbers during the war with the aid of United States industrial expertise. Even in these early days it was recognized that microwaves could heat water in a dramatic fashion, and domestic and commercial appliances for heating and cooking foodstuffs began to appear in the United States in the 1950's. The widespread domestic use of microwave ovens occurred during the 1970's and 1980's as a result of effective Japanese technology transfer and global marketing. The purpose of this review is to explain, in a chemically intelligible

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* This review was developed from the Tilden lecture presented by Michael Mingos in London on 6th December, 1989 and in Edinburgh on 31st October, 1989.

[1] W. L. Jolly, 'The Synthesis and Characterisation of Inorganic Compounds', Prentice Hall, 1970.

[2] A. F. Harvey, 'Microwave Engineering', Academic Press, New York, 1963.

fashion, the origins of microwave dielectric heating effects and describe some recent applications to problems in synthetic chemistry. Although microwave spectroscopy forms a common component of the great majority of undergraduate chemical courses, microwave dielectric heating effects are generally neglected. In our opinion this lack of definition between the two subjects has resulted in the relative neglect of the chemical applications of microwave heating effects. While the mass production of microwave ovens has made them readily available at a cheap price their utilization in chemical laboratories has been sparse.

2 Microwaves and their Interactions with Matter

The microwave region of the electromagnetic spectrum (see Figure 1) lies between infra-red radiation and radio frequencies and corresponds to wavelengths of 1 cm to 1 m (frequencies of 30 GHz to 300 MHz respectively). The wavelengths between 1 cm and 25 cm are extensively used for RADAR transmissions and the remaining wavelength range is used for telecommunications. In order not to interfere with these uses, domestic and industrial microwave heaters are required to operate at either 12.2 cm (2.45 GHz) or 33.3 cm (900 MHz) unless the apparatus is shielded in such a way that no radiation losses occur. Domestic microwave ovens generally operate at 2.45 GHz.

Since some confusion may persist in the mind of chemists concerning the distinction between microwave spectroscopy and microwave dielectric heating effects the differences will be discussed in some detail below. In microwave spectroscopy molecules are studied in the gas phase and the microwave spectrum of a molecule shows many sharp bands[3] in the frequency range 3—60 GHz. The sharp bands in the spectrum arise from transitions between quantized rotational states of the molecule defined by the following relationship:

$$\text{Rotational energy, } E_\mathrm{j} = J(J + 1)h^2/8\pi I^2$$

where J is the rotational quantum number, I is the moment of inertia and h is Planck's constant. In order to observe a pure rotational spectrum an oscillating dipole has to be associated with the molecular rotation. To a first approximation this corresponds to the molecule possessing a permanent dipole moment.[4]

The microwave spectra of small molecules are sharp and lines less than 1 MHz apart can often be distinguished. Therefore, microwave spectroscopy provides an excellent fingerprinting technique for identifying molecules in the gas phase and has, for example, been used to confirm the presence of a wide range of molecules in outer space. Additionally, the accurate B values $[B = j/(8\pi^2 Ic)]$ available can, by the judicious application of isotopic substitution, lead to the precise determination of bond lengths and angles. Isotopic substitution has also led to the determination of some of the most accurate estimates of relative atomic masses. The departure of the molecule from the ideal rigid rotator can be studied

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[3] G. Herzberg, 'Infrared and Raman Spectra', van Nostrand, Princeton, 1945.

[4] C. N. Banwell, 'Fundamentals of Molecular Spectroscopy', 3rd edn., McGraw-Hill, Maidenhead, 1983.

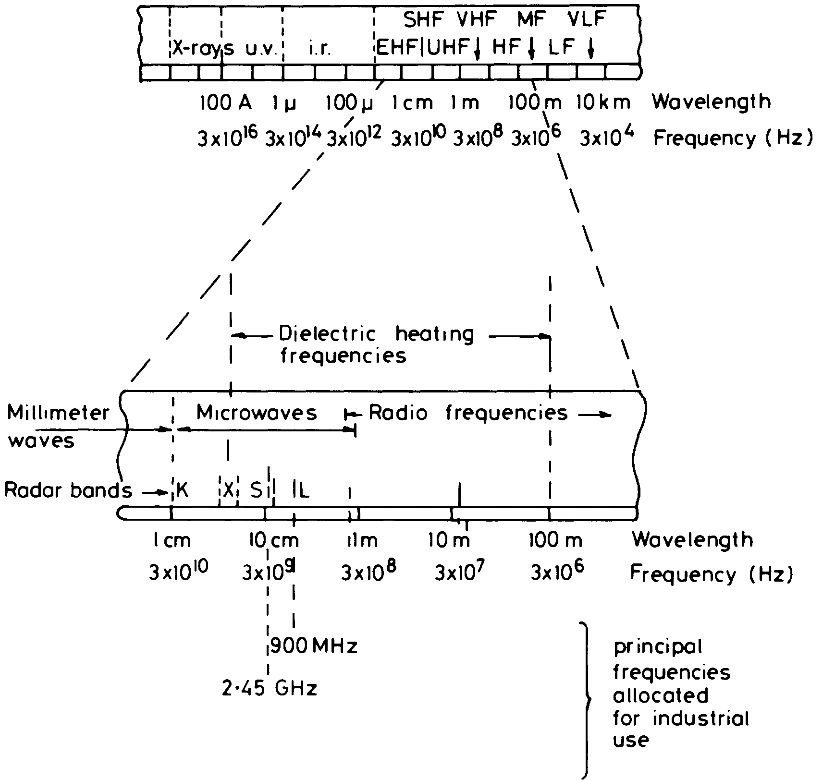

Figure 1 *The electromagnetic spectrum indicating the important microwave frequencies for dielectric heating*

by the evaluation of the distortion constants D_J and $D_{J,K}$, leading to calculations of approximate force constants, and the application of the Stark effect allows the determination of precise values of molecular dipole moments.

In the gas phase, at low pressure, the lifetime of the excited state produced by exciting a particular rotational state is long. However, as a consequence of Heisenberg's uncertainty principle at pressures of around 10^{-1} mmHg the reduction in the lifetime due to collisions broadens the spectral peaks. In liquids and solids, where the molecules are generally not free to rotate independently, the spectra are too broad to be observed. It is to these phases that microwave dielectric loss heating effects are relevant and need to be distinguished from the spectroscopic effects. A material can be heated by applying energy to it in the form of high frequency electromagnetic waves. The origin of the heating effect produced by the high frequency electromagnetic waves arises from the ability of an electric field to exert a force on charged particles. If the particles present in the substance can move freely through it, then a current has been induced. However, if the charge carriers are bound to certain regions they will move until a counter force balances them and the net result is a dielectric polarization. Both conduction and dielectric polarization are sources of microwave heating and we will deal with them in turn. The microwave heating effect depends on the frequency as well as the power applied, but unlike microwave spectroscopy the effect does not result from well spaced discrete quantized energy states, but with a broad band bulk phenomenon which can be treated classically.

The theory of microwave heating has been developed by many workers, amongst them Debye,[5] Frohlich,[6] Daniel,[7] Cole and Cole,[8] Hill,[9] and Hasted.[10] A detailed analysis is beyond the scope of this review. We shall nevertheless discuss the important principles and indicate their chemical significance.

A. Dielectric Polarization.—One source of microwave dielectric heating lies in the ability of an electric field to polarize charges in a material and the inability of this polarization to follow rapid reversals of an electric field.

The total polarization is the sum of a number of individual components:

$$\alpha_t = \alpha_e + \alpha_a + \alpha_d + \alpha_i$$

where, α_e, the electronic polarization, arises from the realignment of electrons around specific nuclei; α_a, the atomic polarization, results from the relative displacement of nuclei due to the unequal distribution of charge within the molecule; α_d is the dipolar polarization, resulting from the orientation of permanent dipoles by the electric field; and α_i is the interfacial polarization, or Maxwell–Wagner effect, which occurs when there is a build up of charges at interfaces.

With an oscillating electric field, such as that associated with electromagnetic radiation, the response of a material depends on the time scales of the orientation and disorientation phenomena relative to the frequency of the radiation. The timescales for the polarization and depolarization of α_e and α_a are much faster than the microwave frequencies and therefore these effects do not contribute to the dielectric heating effect. In contrast the timescales for polarization associated with the permanent dipole moments in the molecule, α_d, and possibly the timescale associated with some interfacial processes, α_i, are comparable to microwave frequencies. Consequently it is these effects that require further explanation.

(i) *Dipolar Polarization*, α_d. Dipolar polarization, such as that excited in liquid water, is due to its dipole moment which in turn results from the differing electronegativities of the oxygen and hydrogen atoms. At low frequencies the time taken by the electric field to change direction is longer than the response

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[5] P Debye, Polar Molecules, *Chemical Catalog*, New York, 1929

[6] H Frohlich, 'Theory of Dielectrics', 2nd edn , Oxford University Press, London, 1958

[7] V Daniel, 'Dielectric Relaxation', Academic Press, New York, 1967

[8] K S Cole and R H Cole, *J Chem Phys*, 1941, **9**, 341

[9] N Hill, W E Vaughan, A H Price, and M Davies, 'Dielectric Properties and Molecular Behaviour', von Nostrand, New York, 1969

[10] J B Hasted, 'Aqueous Dielectrics', Chapman and Hall, London, 1973

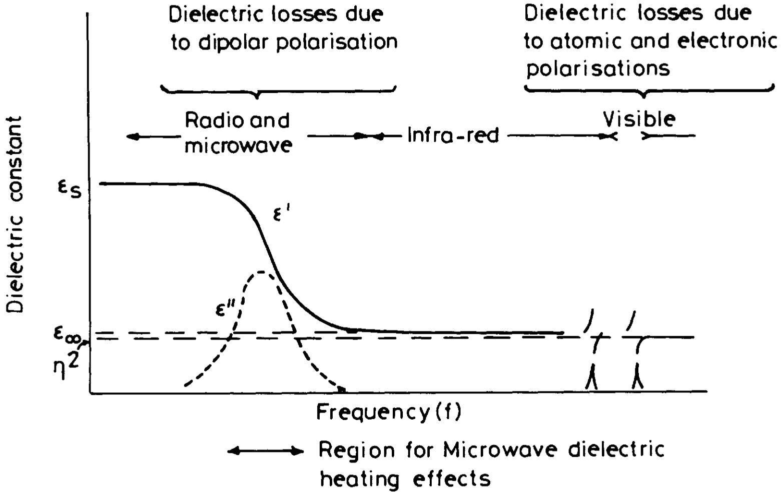

Figure 2 *Schematic illustration of the real and imaginary components of the dielectric constant,* ε' *and* ε''*, as a function of frequency*

time of the dipoles, and the dielectric polarization keeps in phase with the electric field. The field provides the energy necessary to make the molecules rotate into alignment. Some of the energy is transferred to the random motion each time a dipole is knocked out of alignment and then realigned. The transfer of energy is so small, however, that the temperature hardly rises. If the electric field oscillates rapidly, it changes direction faster than the response time of the dipoles. Since the dipoles do not rotate, no energy is absorbed and the water does not heat up.

In the microwave range of frequencies the time in which the field changes is about the same as the response time of the dipoles. They rotate because of the torques they experience, but the resulting polarization lags behind the changes of the electric field. When the field is at a maximum strength, say in the upward direction, polarization may still be low. It keeps rising as the field weakens. The lag indicates that the water absorbs energy from the field and is heated.

Two parameters define the dielectric properties of materials and are used extensively in this review. The first, ε', the dielectric constant describes the ability of the molecule to be polarized by the electric field. At low frequencies this value will reach a maximum as the maximum amount of energy can be stored in the material. The dielectric loss, ε'', measures the efficiency with which the energy of the electromagnetic radiation can be converted into heat. The manner in which ε' and ε'' vary with frequency are shown schematically in Figure 2.[11] The dielectric loss goes through a maximum as the dielectric constant falls. The ratio of the dielectric loss and the dielectric constant define the (dielectric) loss tangent =

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[11] A. C. Metaxas and R. J. Meredith, 'Industrial Microwave Heating', Peter Perigrinus, London, 1983.

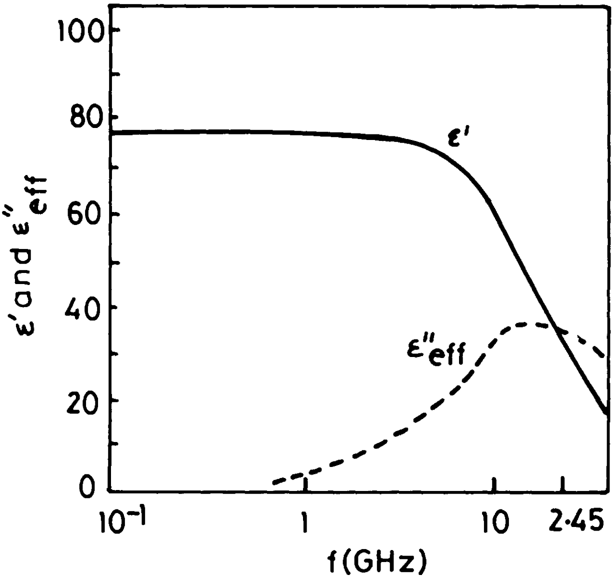

Figure 3 *Dielectric properties of water as a function of frequency*

$\varepsilon''/\varepsilon' = \tan\delta$, which defines the ability of a material to convert electromagnetic energy into heat energy at a given frequency and temperature.

The time taken for the dipoles in water to become polarized and then depolarized is governed by a relaxation time constant. Only when this time constant approaches the inverse excitation frequency will a particular polarization mechanism become important. Note that since the time constants for electronic and atomic polarization are much faster than 10^{-9} s these mechanisms do not contribute to microwave dielectric heating effects.

In Figure 3 the dielectric properties of distilled water are plotted as a function of frequency at 25 °C.[12] It is apparent that appreciable values of the dielectric loss exist over a wide frequency range. Note that the greatest heating as measured by ε'' reaches its maximum at around 20 GHz while domestic microwave ovens operate at a much lower frequency, 2.45 GHz. The practical reason for the lower frequency is that it is necessary to heat food efficiently throughout its interior. If the frequency is optimal for maximum heating rate, the microwaves are absorbed in the outer regions of the food, and penetrate only a short distance. Thus the penetration depth, *i.e.* the depth into a material where the power falls to one half its value on the surface, is another important parameter in the design of a microwave experiment. An approximate relationship for penetration depth D_p, when ε'' is small, is given by:

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[12] A. R. von Hippel, 'Dielectric Materials and Applications', MIT Press, 1954.

$$D_p \propto \lambda_0\sqrt{(\varepsilon'/\varepsilon'')}$$

where λ_0 is the wavelength of the microwave radiation.

The theoretical examination of the frequency dependence of ε' and ε'' began with the derivation of the Debye equations:[5,13]

$$\varepsilon'_d = \varepsilon'_\infty + \frac{(\varepsilon'_0 - \varepsilon'_\infty)}{(1 + \omega^2\tau^2)}$$

$$\varepsilon''_d = \frac{(\varepsilon'_0 - \varepsilon'_\infty)\omega\tau}{(1 + \omega^2\tau^2)}$$

where ε'_∞ and ε'_0 are defined as the high frequency and static dielectric constants, and ω and τ are the frequency and relaxation times which characterize the rate of build up and decay of polarization. The above results apply to both liquids and solids though different models are used to derive it. It is an interesting feature of the Debye equations that the values of ε'_d and ε''_d at the frequency at which the dielectric loss is a maximum is independent of this frequency and of the relaxation time:

$$\varepsilon''_{max} = (\varepsilon'_0 - \varepsilon'_\infty)/2 \text{ where } \varepsilon'_d = (\varepsilon'_0 + \varepsilon'_\infty)/2$$

In liquids it is generally assumed that the dipoles can point in any direction and are continually changing due to thermal agitation.[6] Debye's interpretation of the relaxation is given in terms of the frictional forces in the medium. Using Stokes' theorem[14] he derived the following expression for the relaxation time of spherical dipoles:

$$\tau = 4\pi r^3\eta/kT$$

where η is the viscosity of the medium, r the radius of the dipolar molecule and k Boltzman's constant.

In solids due to the variable interaction of a molecule with its neighbours a dipole has a number of equilibrium positions. They are separated by potential barriers over which the dipole must pass in turning from one direction to another. In the simplest case only two equilibrium positions with opposite dipole directions exist and they are separated by an energy barrier U_a as shown in Figure 4. From Boltzman statistics it follows that the number of transitions from one state to another is proportional to $(1 - e^{t/\tau})$ where t is the time and τ the relaxation time constant. This leads to the following relationship between time constant and dielectric constant:

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[13] P Debye, *Phys Z*, 1935, **36**, 100

[14] M A Lauffer, *J Chem Educ*, 1981, **58**, 250

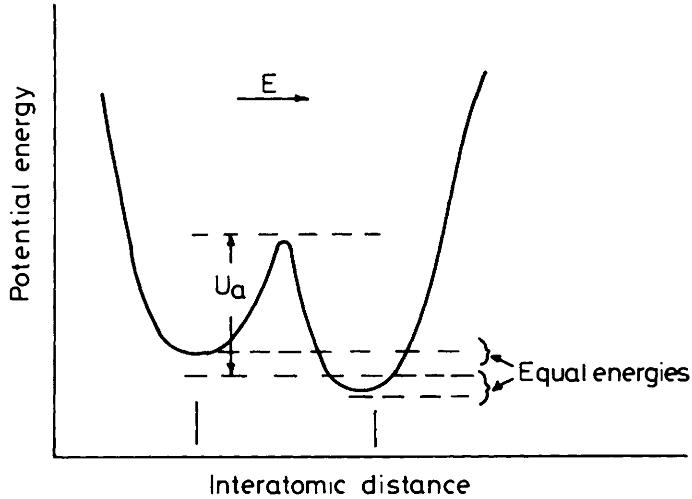

Figure 4 *Potential energy diagram for two alternative positions of a dipole relative to an electric field*

$$\tau = \frac{e^{U_a/kT}(\varepsilon_0' + 2)}{n(\varepsilon_\infty' + 2)}$$

where $1/n$ is the time for a single oscillation in the potential well. The magnitude of the absorption for this model has been discussed by Frohlich who concluded that the expressions should be equivalent to those followed by liquids.[6] The following form of the Onsager equation[15] has been shown to apply to many liquids and solids:[16–18]

$$\varepsilon_0' - \varepsilon_\infty' = \frac{4\pi N m^2 \varepsilon_0'(\varepsilon_\infty' + 2)^2}{9kT(2\varepsilon_0' + \varepsilon_\infty')}$$

where N is the number of molecules and m their mass. Note that in such a system the magnitude of the dielectric absorption decreases with increasing temperature.

In practice it is found that many polar solids, *e.g.* aliphatic long chain ketones and most ethers, have small dielectric losses. This arises because in the solid state the energy differences between the equilibrium positions of the dipoles are very large. In most other cases, *e.g.* many long-chain esters and some ethers, there is significant dielectric absorption at room temperatures which decreases with increasing temperature in agreement with the Onsager equation. The dielectric properties of some common solvents are given in Table 1.[12] The high dielectric losses of the alcohols are particularly noteworthy.

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[15] C J F Bottcher, 'Theory of Electric Polarisation', Elsevier, Amsterdam, 1952

[16] R J Meakins, *Trans Faraday Soc*, 1955, **51**, 953

[17] C P Smyth, 'Dielectric Behaviour and Structure', McGraw-Hill, New York, 1955

[18] R J Meakins, *Trans Phys Soc*, 1956, **52**, 320

Table 1 *Dielectric properties of common solvents*[12]

	Frequency					
	3×10^8 Hz		3×10^9 Hz		1×10^{10} Hz	
Solvent	ε'	ε''	ε'	ε''	ε'	ε''
Water	77.5	1.2	76.7	12.0	55.0	29.7
0.1 M NaCl	76	59	75.5	18.1	54	30
Heptane	1.97		1.97	2×10^{-4}	1.97	3×10^{-3}
Methanol	30.9	2.5	23.9	15.3	8.9	7.2
Ethanol	22.3	6.0	6.5	1.6	1.7	0.11
n-Propanol	16.0	6.7	3.7	2.5	2.3	0.20
n-Butanol	11.5	6.3	3.5	1.6	0.2	
Ethylene glycol	39	6.2	12	12	7	5.5
Carbon tetrachloride	2.2		2.2	9×10^{-4}	2.2	3×10^{-3}

Many liquids and solids give dielectric loss curves much wider than a Debye curve, due to the presence of a range of relaxation times. Frequently this variation can be represented by the Fuoss and Kirkwood empirical expression:[19]

$$\varepsilon'' = \varepsilon''_{\max}\operatorname{sech}[b\{\ln(f/f_{\max})\}]$$

The value of b varies between one for a single relaxation and zero for an infinite number, f is the frequency and $f_{\max}$ the frequency of maximum loss.

(ii) *Interfacial Polarization.* A suspension of conducting particles in a non-conducting medium is an inhomogeneous material whose dielectric constant is frequency dependent. The loss relates to the build up of charges between the interfaces and is known as the Maxwell–Wagner effect. Its importance in the microwave region has not been well defined. Absorption centred around a frequency of 10^7 Hz may tail into this frequency range. Wagner[20] has shown that for the simplest model featuring this type of polarization, consisting of conducting spheres distributed through a non-conducting medium, the dielectric loss factor, of volume fraction v of material, is given by:

$$\varepsilon''_1 = \frac{9v\varepsilon' f_{\max}}{1.8 \times 10^{10}\sigma}\;\frac{(\omega\tau)}{(1 + \omega^2\tau^2)}$$

where, σ is the conductivity (in Sm^{-1}) of the conductive phase and ε' its dielectric constant. The frequency variation of the loss factor is similar to that of dipolar relaxation. An experimental system approximating to Wagner's model has been made by incorporating up to 3 per cent of roughly spherical particles of

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[19] R. M. Fuoss and J. G. Kirkwood, *J. Am. Chem. Soc.*, **63**, 385.

[20] K. W. Wagner, *Arch. Elektrotech.*, 1914, **2**, 371.

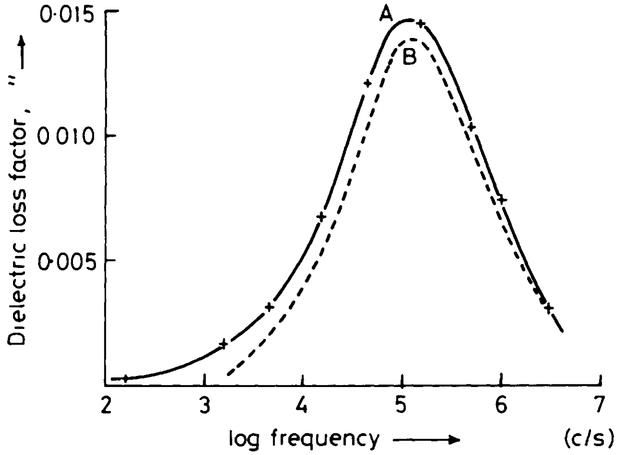

Figure 5 *Dielectric absorption for a Maxwell–Wagner system consisting of spherical conducting particles of copper phthalocyanine in paraffin wax. Curve* A. 0.62% (*volume*) *of copper phthalocyanine spheres, curve* B· *theoretical*[21]

semiconducting copper phthalocyanine into paraffin wax.[21] This gave good agreement with the theory as shown in Figure 5.

B. Conduction Losses.—As the concentration of the conducting phase dispersed in a non-conducting phase is increased there comes a point where some account has to be made of the interactions between individual conducting areas. This can be viewed as an extension of simple Wagner theory.[10,22–24] A general approach to interfacial polarization has been considered by Maxwell and Wagner in their two layer capacitor model as shown in Figure 6.

Thus the total Maxwell–Wagner effect is seen to be a composite produced by areas of differing dielectric constants and conductivity. The complex permittivity is found to be equal to:

$$\varepsilon_r^* = \varepsilon'_\infty + \frac{(\varepsilon'_0 - \varepsilon'_\infty)}{(1 + j\omega t)} - \frac{j\sigma}{\omega\varepsilon_0}$$

The real part is precisely that given by the simple Debye theory. The loss term not only gives a single relaxation time response but also a term due to d.c. conductivity. The contribution to the total loss due to this extra conductive part depends on the d.c. conductivity itself. For highly conductive liquids and solids, particularly those containing large amounts of salts, there comes a point where the conductive loss effects are larger than the dipolar relaxation effects.

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[21] B V Hamon, *Aust J Phys*, 1953, **6**, 304

[22] M M Z Kharadly and W Jackson, *Proc Institute of Electrical Engineers*, 1953, **100**, 199

[23] J C Anderson, 'Dielectrics', Chapman and Hall, London, 1964

[24] R Coelho, 'Physics of Dielectrics for the Engineer', Elsevier Publishing Co, Amsterdam, 1979

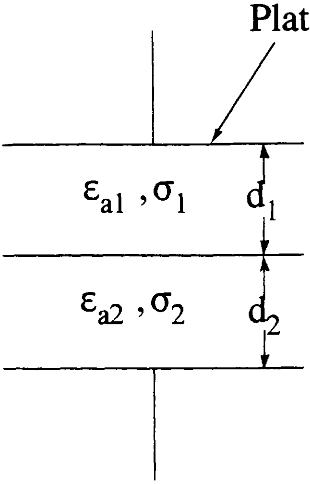

Figure 6 *The Maxwell–Wagner two layer capacitor* (ε_{ax} *and* σ_x *refer to dielectric constant and conductivity,* d_x *is the distance*)

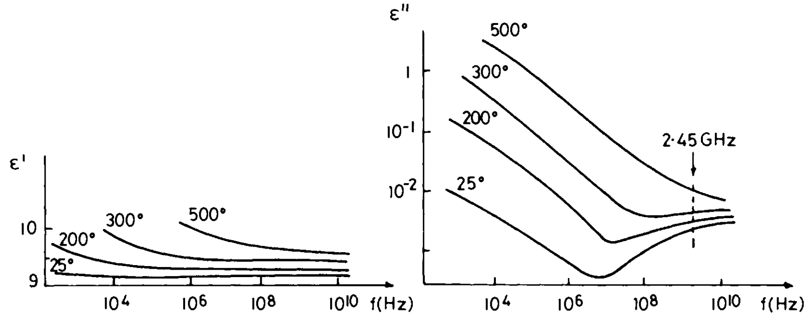

Figure 7 *Dielectric properties as a function of frequency and temperature for sintered alumina*[24]

In Figure 7 the dielectric loss for sintered alumina[25] as a function of temperature is illustrated. At room temperature the conduction loss effects are important only at lower frequencies. Losses in the microwave region are due to dipolar relaxation. However as the temperature increases conduction losses increase rapidly and become as important as dipolar relaxation loss in the microwave region.

The increase of conduction with temperature in alumina is associated with the thermal activation of the electrons which pass from the oxygen 2*p* valence band to the 3*s*3*p* conduction band. In addition, electrical conduction is generally enhanced by material defects which sharply decrease the energy gap between the valency and conduction bands.

[25] A. J. Berteaud and J. C. Badot, *J. Microwave Power*, 1976, **11**, 315.

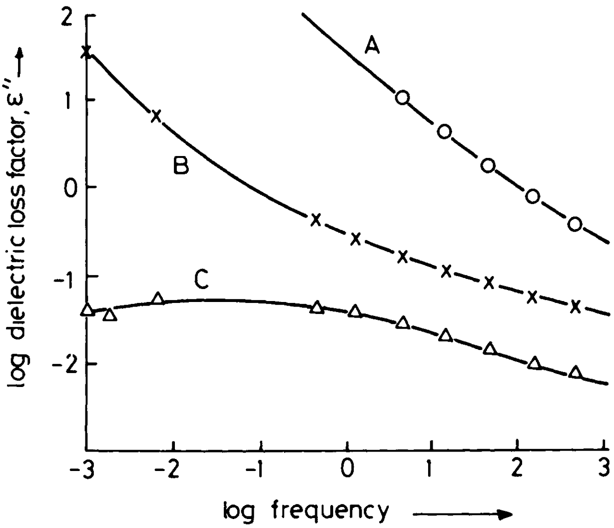

Figure 8 *DC conductivity and Maxwell–Wagner absorption due to a conducting powder in paraffin wax. Curves* A, B, *and* C 1.9, 0.62, 0.19% (*volume*) *respectively, copper phthalocyanine*[21]

Attempts have been made to represent the conduction losses through the expression:

$$\varepsilon_c'' = \sigma/\omega\varepsilon_0$$

and Hamon[21] has again simulated this behaviour with rather higher concentrations of copper phthalocyanine in paraffin wax (see Figure 8). At high frequencies the loss is often greater than that suggested by a linear relationship, and expressions of the type:

$$\varepsilon_c'' = \text{constant}.f^{\,k}$$

where k approaches unity for high concentrations of conducting material, are found to be more appropriate.[26]

3 Microwave Heating of Liquids and Solids

The rate of rise of temperature due to the electric field of microwave radiation is determined by the following equation:[27]

$$\frac{\delta T}{\delta t} = \frac{\text{constant}\ \varepsilon'' f E_{\text{rms}}^2}{\rho C_p} \qquad (1)$$

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[26] L K H van Beek, *Prog Dielec*, 1967, 7, 69

[27] T T Meek, *J Mat Sci Lett*, 1987, **6**, 638

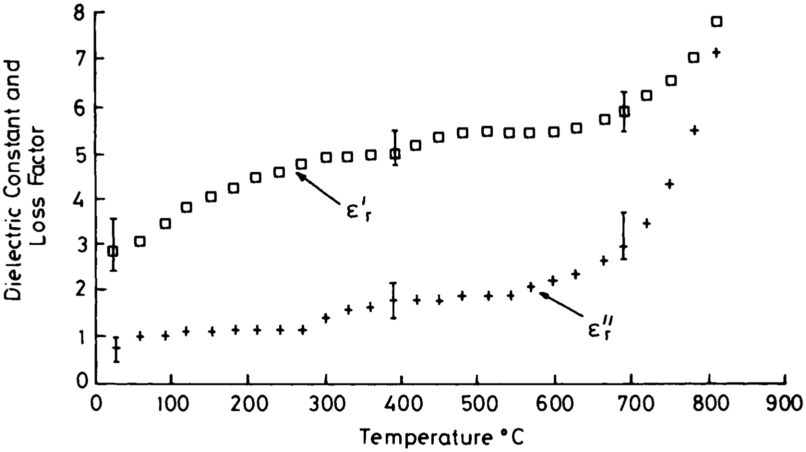

Figure 9 *The dielectric properties of* CuO *as a function of temperature*[30]

where E^2_{rms} is the r.m.s. field intensity, ρ the density, and C_p the specific heat capacity. The losses due to radiation[28] are governed by:

$$\frac{\delta T}{\delta t} = \frac{-e\alpha}{\rho C_p}\left(\frac{\text{area}}{\text{volume}}\right)_{\text{sample}} T^4$$

where e is the sample emissivity, and α the Stefan–Boltzmann constant. The resulting temperature rise is thus determined by the dielectric loss, specific heat capacity, and emissivity of the sample as well as the strength of the applied field. These physical properties of the liquid or solid samples are all temperature dependent, making the complete theoretical analysis of dielectric heating mathematically very complex.

The dielectric constant and dielectric loss values have been established for a number of materials at room temperature. The largest collection of data is that due to von Hippel[12,29] though many of these data apply to foodstuffs and are of limited use to the chemist. The study of dielectric constant and dielectric loss as a function of temperature is less well developed, particularly in solids, where data are needed up to sintering temperatures (1000—2200 °C). The data in Figure 9 on the dielectric properties of CuO as a function of temperature[30] comprise one of the few examples of a detailed and complete study.

Several workers have, however, reported the temperatures reached by liquids and solids when placed in conventional microwave ovens. Some of the available data for liquids and solids are given in Tables 2 and 3 respectively.[31,32]

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[28] K. A. Alberty, 'Physical Chemistry', 7th edn., Wiley, New York, 1987, 326.

[29] A. R. von Hippel, 'Dielectrics and Waves', MIT Press, 1954.

[30] W. R. Tinga, *Electromag. Energy Rev.*, 1988, **1**, 1.

[31] R. N. Gedye, F. E. Smith, and K. G. Westaway, *Can. J. Chem.*, 1988, **66**, 17.

[32] S. L. McGill and J. W. Walkiewicz, *J. Microwave Power Electromag. Energy, Symp. Summ.*, 1987, 175.

Table 2 *The temperature of* 50 ml *of several solvents after heating from room temperature for* 1 min *at* 560 W, 2 45 GHz

Solvent	*T*/°C	b p °C	*Solvent*	*T*/°C	b p °C
Water	81	100	Acetic acid	110	119
Methanol	65	65	Ethyl acetate	73	77
Ethanol	78	78	Chloroform	49	61
1-Propanol	97	97	Acetone	56	56
1-Butanol	109	117	DMF	131	153
1-Pentanol	106	137	Diethyl ether	32	35
1-Hexanol	92	158	Hexane	25	68
1-Chlorobutane	76	78	Heptane	26	98
1-Bromobutane	95	101	CCl_4	28	77

Table 3 *Effect of microwave heating on the temperatures of solids* (*all experiments begin at room temperature*)
Column A 25 g *samples in a* 1 kW *oven* (2 45 GHz) *with a* 1000 ml *vented water load*
Column B 5—6 g samples in a 500 W *oven*

A			*B*		
Chemical	*T*/°C	*t*/min	*Chemical*	*T*/°C	*t*/min
Al	577	6	CaO	83	30
C	1283	1	CeO_2	99	30
Co_2O_3	1290	3	CuO	701	0 5
CuCl	619	13	Fe_2O_3	88	30
$FeCl_3$	41	4	Fe_3O_4	510	2
$MnCl_2$	53	1 75	La_2O_3	107	30
NaCl	83	7	MnO_2	321	30
Ni	384	1	PbO_2	182	7
NiO	1305	6 25	Pb_3O_4	122	30
$SbCl_3$	224	1 75	SnO	102	30
$SnCl_2$	476	2	TiO_2	122	30
$SnCl_4$	49	8	V_2O_5	701	9
$ZnCl_2$	609	7	WO_3	532	0 5

The strength of the applied field E^2_{rms} in equation 1 is related to the applied power The effect of applied power on the rate of microwave heating is illustrated in Figure 10 for samples of 1-propanol[31] As expected, a larger power leads to a larger E^2_{rms} and hence a greater heating rate

Temperature measurement inside the microwave cavity is complicated by the presence of an intense electric field[33] Thus thermocouples must be efficiently shielded and grounded to avoid sparking These considerations are particularly important when volatile and inflammable solvents are being heated in the cavity For temperatures up to 450 °C fibre optic thermometers have been successfully applied[34] Surface temperatures up to 3000 °C can be measured remotely using

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[33] W R Tinga, *MRS Symp Proceed*, 1986, **60**, 105

[34] R R Bowman, *IEEE Trans Microwave Theory Techn*, 1976, MTT-24 43

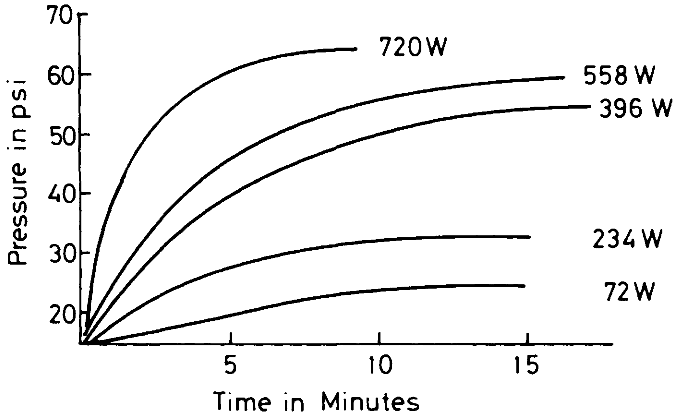

Figure 10 *The effect of applied power on the heating rate of samples of 1-propanol*

infra-red pyrometry, though substantial differences exist between surface and internal temperatures, particularly at the higher temperatures.

4 The Microwave Oven

The principal features of a modern microwave oven are illustrated in the cutaway diagram shown in Figure 11.

The important features of the magnetron in which the microwaves are generated, are shown in Figure 12. A magnetron is a thermionic diode having an anode and a directly heated cathode. As the cathode is heated, electrons are released and are attracted towards the anode. The anode is made up of an even number of small cavities, each of which acts as a tuned circuit. The gap across the end of each cavity behaves as a capacitance. The anode is therefore a series of circuits which are tuned to oscillate at a specific frequency or its overtones.

A very strong magnetic field is induced axially through the anode assembly and has the effect of bending the path of the electrons as they travel from the cathode to the anode. As the deflected electrons pass through the cavity gaps they induce a small charge into the tuned circuit, resulting in the oscillation of the cavity. Alternate cavities are linked by two small wire straps (mode straps) which ensure the correct phase relationship. This process of oscillation continues until the oscillation has achieved a sufficiently high amplitude. It is then taken off the anode *via* an antenna. Of the 1200 W of electrical line power used by the magnetron around 600 W is converted into electromagnetic energy. The remainder is converted into heat that must be dissipated through air or water cooling.

The variable power available in domestic ovens is produced by switching the magnetron on and off according to a duty cycle. For example a typical 600 W oven with a 30 s duty cycle can be made to deliver an average of 300 W by switching the magnetron on and off every 15 s. Large duty cycles are undesirable

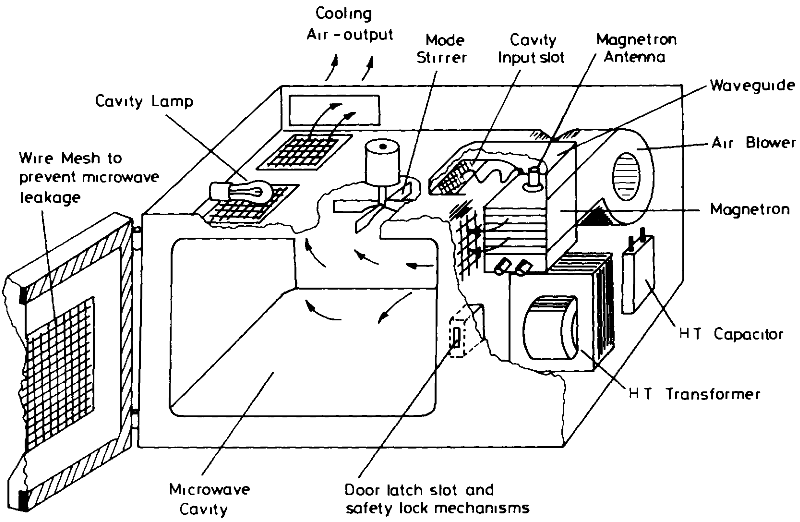

Figure 11 *The major features of a modern domestic microwave oven*

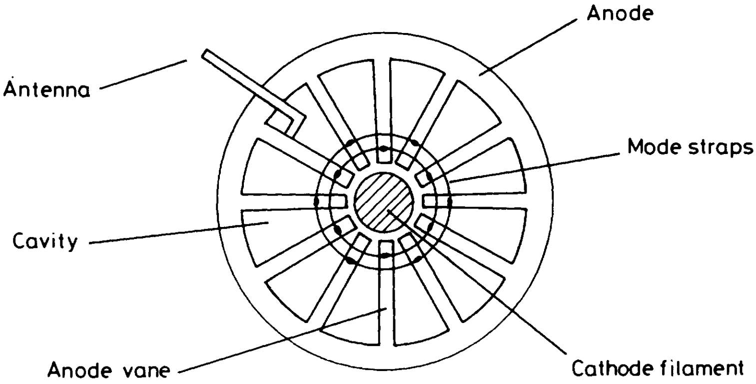

Figure 12 *Schematic illustration of a magnetron*

in chemical applications where samples may cool dramatically between switching steps and this is, therefore, one factor which must be considered in adapting an oven for chemical applications.

A waveguide is a rectangular channel made of sheet metal. Its reflective walls allow the transmission of microwaves from the magnetron to the microwave cavity or applicator. The minimum frequency which can be propagated is related to the dimensions of the rectangular cross section through the expression $c/f = 2d$ where c is the speed of light, f the cut-off frequency and d the larger of the dimensions of the rectangular section of the waveguide.

The reflective walls of the microwave cavity are necessary to prevent leakage of radiation and to increase the efficiency of the oven. There is rarely a perfect match between the frequency used and the resonant frequency of the load, so if the energy is reflected by the walls, absorbance is increased because the energy passes through the sample more often and can be partially absorbed on each passage. This can be particularly important if the sample is dimensionally small. If too much energy is reflected back into the waveguide the magnetron may be damaged. Most commercial ovens are protected by an automatic cut-off and there may also be protection in the form of a circulator which directs reflected energy into a dummy load. When working with small loads, poorly absorbing loads or at high powers, a dummy load, for example a beaker of water, should always be placed in the cavity along with the sample to absorb the excess energy.

In the absence of any smoothing mechanism the electric field pattern produced by the standing waves set up in the cavity may be extremely complex. Some areas may receive large amounts of energy while others may be almost neglected. To ensure that the incoming energy is smoothed out in the cavity a mode stirrer (a reflective, fan-shaped paddle) is sometimes used. Most microwave ovens are also supplied with a turntable, which ensures that the average field experienced by the sample is approximately the same in all directions.

When the liquids or solids which are being heated are poor absorbers of microwave energy and are only available in small amounts, the multi-mode microwave oven no longer represents the most effective system. This is particularly a problem if the samples need to be heated to a high temperature in a controlled fashion. A more expensive experimental set-up has to be used wherein a single mode resonant cavity is tuned to the characteristics of the material being heated. The main features of this type of apparatus are shown in the form of a block diagram in Figure 13. It has been used to process poorly absorbing polymers.[35]

Briefly a single-mode resonant heater allows a sample to be placed at positions of much higher electric field strengths than can be obtained in a multimode oven. Having chosen a particular resonant mode or electric field distribution pattern insertion of the sample into the cavity changes the resonant frequency. By varying the position of the plunger the cavity can be made to resonate at the working frequency. Additionally the coupling iris is altered in size to ensure a good impedance match between the waveguide and the cavity so that the energy is not reflected back towards the source. The efficiency of the matching can be followed either by measuring the standing wave ratio in a slotted line or by using a network analyser. Since the dielectric properties of the material depend on temperature the matching requirements of the cavity are continually changing and are usually controlled by a computer. The circulator protects the magnetron source from the high reflected powers that exist when there is a poor energy match. Use of a resonant cavity increases the effective cavity power by three

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[35] M. Teffal and A. Gourdenne, *Eur. Polym. J.*, 1983, **19**, 543.

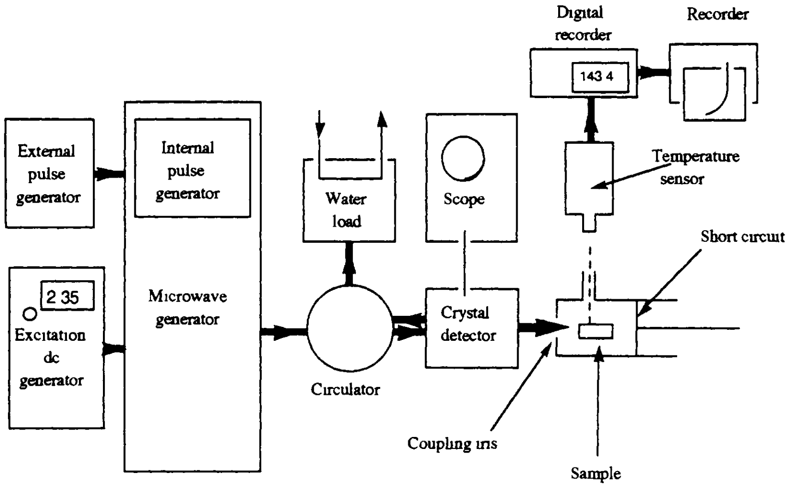

Figure 13 *Single-mode resonant heating system*[35]

orders of magnitude allowing the microwave heating of relatively low-loss materials such as polymers and some ceramics using small powers (<2 5 kW)

5 Reactions Utilizing the Dielectric Loss Properties of Solvents

It is apparent from the discussion in Sections 2 and 3 above that any organic or inorganic solvent with a low molecular weight and a high dipole moment will couple effectively with microwaves at 2 45 GHz The solvents which have been most commonly used for synthetic reactions are H_2O, MeOH, and EtOH Other solvents such as MeCN, DMF, and CH_2Cl_2 couple effectively to microwaves but have been less commonly used Non-polar organic solvents such as C_6H_6, petroleum ethers, and CCl_4 have negligible dielectric loss and therefore do not couple efficiently with microwaves The addition of small amounts of alcohols or water to these solvents can lead to dramatic coupling effects however Hence a 1 4 EtOH toluene mixture can be heated to boiling in a few minutes in a standard domestic microwave oven It should also be emphasized that the presence of salts in polar solvents can frequently enhance dielectric loss effects and microwave coupling

Clearly it is unsafe to heat organic solvents with microwaves in a contained space Sparking induced by the switching of the magnetron could lead to a violent explosion in the microwave cavity Therefore the problem of solvent containment is paramount in the design of safe synthetic procedures

A. Low Pressure Conditions.—Much important work has been performed on the synthesis and processing of polymers using microwave dielectric heating effects Since these materials are not very volatile, containment problems are not great For the synthesis of low molecular weight organic molecules, organometallic, and co-ordination compounds, containment problems are more severe. Some specific applications are given below:

(i) *Synthesis of Polymers.* Typically, polymer solutions and particularly thin films are poor absorbers of microwave radiation. Accordingly resonance cavity techniques have been widely employed in the curing of polymers such as polyurethane systems,[36] epoxy-glass fibre composites,[37] DGEBA-DDM epoxy resins,[38] and epoxy resin-aluminium particle systems.[39]

Early work in this area was concerned with following the evolution of temperature in samples as a function of the applied power.[40] For the cross linking of epoxy resins a model has been developed linking the time dependence of temperature to the applied power and heat losses due to conduction. Further progress has been made by analysing the variations with time of the applied power $P_u = P_u(t)$ degraded as heat inside the samples (dielectric loss) and of the derivatives $T' = \delta T/\delta t$ and $P'_u = \delta P_u/\delta t$ for pure resins and epoxy-glass fibre mixtures.[37]

The role of solvent and polymer in the formation of films has been studied on hollowed, microwave transparent, PTFE.[41] Two series of polymers were investigated: PVAC (polyvinylacetate) as a polar molecule with high dielectric constant, and polystyrene, a non-polar polymer with low dielectric losses. The solvents used were DMF, MEK (methylethylketone) and benzene in order of decreasing polarity. The rate of polymer formation was followed by means of surface temperature measurement. Each solution of polystyrene began to heat according to the overall polarity of the mixture. Then, as solvent evaporated from the mixture, the temperature decreased to approach a final steady state value. With solutions of PVAC more complex behaviour was found, due to the non-additive combination of solvent and polymer losses. For example, MEK solutions of PVAC are less susceptible to microwaves than benzene solutions since some interaction between the two compounds probably restricts the electrical orientation of polar groups.

Improvements in film hardness and some degree of selectivity have been observed in studies using a pulsed microwave source where the on/off repetition frequency is of the order of 1×10^{-3} Hz to 20 KHz. In addition to bulk dielectric heating it is believed that specific molecular dipoles or chain segments can be influenced by using pulsed microwave cycles.

Using FTIR and ^{13}C NMR to study the cross-linking of DGEBA (diglycidyl ether of bisphenol-A) with DDS (4,4′-diaminodiphenylsulphone), it was found that the conversion rate was not a function of the highest temperature reached.[42]

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[36] B. Silinski, C. Kuzmycz, and A. Gourdenne, *Eur. Polym. J.*, 1987, **23**, 273.

[37] A. Gourdenne and Q. LeVan, *Polym. Prepr.*, 1981, **22**, 125.

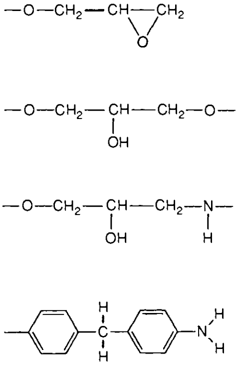
[38] Q. LeVan and A. Gourdenne, *Eur. Polym. J.*, 1987, **23**, 777.

[39] Y. Bazaird and A. Gourdenne, *Eur. Polym. J.*, 1988, **24**, 881.

[40] A. Gourdenne, A. H. Maassarani, P. Monchaux, S. Aussudre, and L. Thourel, *Polym. Prepr.*, 1979, **20**, 471.

[41] H. Julien and H. Valot, *Polymer*, 1983, **24**, 810.

[42] F. M. Thullier, H. Jullien, and M. F. Grenier-Loustalot, *Polymer Commun.*, 1986, **27**, 206.



'pendant chain' with epoxide terminal function; flexible and polar, submitted to double relaxation

flexible and polar

flexible and polar; identical to the segments related to the β-transitions in the cross-linked networks

'pendant chain'; heavy and polar

Figure 14 *Possible sources of segmental relaxation in DGEBA–DDM cross-linking*

It appears that more efficient transfer of microwave energy to dipolar sites can be achieved with specific pulses leading to high conversion rates: 2 × 10^{-3} s (700 W), 193 °C, 56% but 20 × 10^{-3} s (1500 W), 177 °C, 62%. Additionally, a pulsed-microwave treatment with low repetition period (2 × 10^{-3} s) induces the formation of bis-aliphatic ethers by catalysing the homopolymerization reaction, while a longer pulse repetition period (50 × 10^{-3} s) promotes the reaction with amines only. The Persoz hardness of polyurethane films formed from 75% ethyl acetate solutions of Desmodur L75 and Desmophen 800 using pulsed irradiation compares favourably with oven cured films.[43] Thus in general the films are harder (Persoz hardness = 370—380 s) compared with oven cured films (340—360 s) and in the most efficient conditions (1000 W, 50 × 10^{-3} s; or 500 W, 2 × 10^{-3} s) very hard films are obtained (400 s). The cross-linking reaction of DGEBA with DDM[44–46] (4,4′-diaminodiphenylmethane) is favoured by pulse repetition frequencies of 1000, 200, and 23.8 Hz which could correspond, probably in a rather complex fashion, to the series of segments shown in Figure 14.

The cure kinetics of polyimides have recently been studied by conventional and microwave heating.[47] The polamic acid precursor (see Figure 15) was prepared by the room temperature reaction of benzophenone tetracarboxylic acid dianhydride (BDTA) and 3,3′-diaminodiphenylsulphone (DDS) in *N*-methylpyrrolidone (NMP). The extent of the imidization by 85 W of 2.45 GHz radiation was studied by FTIR. The equation for the kinetics of imidization can be expressed, at low initial concentrations, as:

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[43] H Jullien and H Valot, *Polymer*, 1985, **26**, 506

[44] N Beldjoudi, A Bouazizi, D Doubi, and A Gourdenne, *Eur Polym J*, 1988, **24**, 49

[45] N Beldjoudi and A Gourdenne, *Eur Polym J*, 1988, **24**, 53

[46] N Beldjoudi and A Gourdenne, *Eur Polym J*, 1988, **24**, 265

[47] D A Lewis, T C Ward, J S Summers, and J E McGrath, 'First Australian Symposium on Microwave Power Applications', Wollongong, 1989

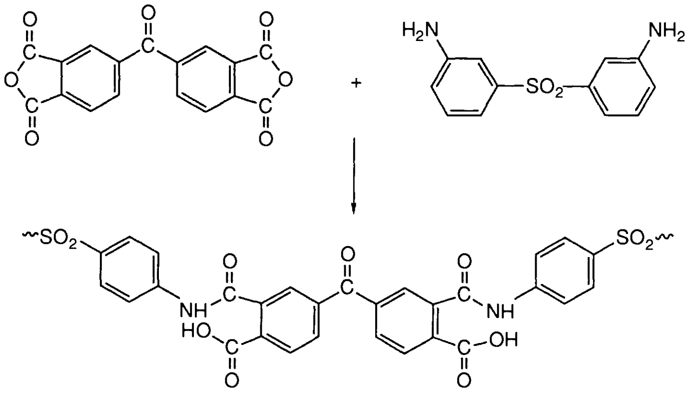

Figure 15 *Synthesis of the polyamic acid precursor*

Table 4 *Rate constants for thermal and solution imidization*[47]

T/°C	$k_{thermal}$/min^{-1}	$k_{microwave}$/min^{-1}
130		0.030
140	0.0014	
149	0.0022	
150		0.076
160		0.103
161	0.0055	
170	0.011	
175		0.169

$$\text{rate} = kf[\text{polymer}]$$

where f is the fraction of unreacted amic acid in the polymer determined directly from the FTIR by taking the ratio of the peak height (relative to a reference peak) to the maximum peak height.

The rate constants determined for the microwave solution imidization in Table 4 indicate that the reaction proceeds rapidly with half lives varying from 23 to 4 minutes for 130 to 175 °C respectively. Furthermore, a comparison of the reaction rate constants for microwave and thermal processing at 150 and 160 °C indicate a significant enhancement in the rate of reaction when electromagnetic processing is employed. At 150 °C there is a 35 fold enhancement. However, this decreases to a 20 fold enhancement at 160 °C.

The authors have suggested two mechanisms for the observed rate acceleration. There is either some specific effect on the NMP coordinated with the amic acid or a very localized temperature rise of say 40—60 °C due to directed absorption of the microwave radiation close to the reaction site.

(ii) *Synthesis of Transition Metal Compounds.* For simple chemical reactions in polar solvents, where it is desirable to limit the pressure to one atmosphere conditions, a reflux procedure has been described.[48] This procedure can be introduced by modifying a conventional microwave oven as illustrated in Figure 16. The conventional chemical reflux system cannot be introduced into the microwave cavity because the circulating water coolant would absorb microwaves strongly and itself heat up rapidly. Furthermore, an air condenser would not be effective in returning the flammable solvents to the reaction flask in a safe manner. One solution to the problem would be to use a coolant that does not absorb microwaves strongly, *e.g.* a non-polar organic or inorganic solvent. An alternative strategy is to locate the water cooled reflux condenser outside the microwave cavity. The condenser is connected to the reaction vessel by means of a port in the microwave cavity that ensures microwave leakage is kept to a safe limit.

In the modification illustrated in Figure 16 the solution is contained within a glass round bottomed flask, which is connected *via* ground glass joints, to an air condenser. The condenser passes through a copper tube bolted to the side of a conventional microwave oven and is then connected to the water condenser, which is located completely outside the oven. This allows the solutions to heat rapidly when the microwave source is switched on and reflux safely without a build up of pressure and the release of volatile inflammables into the atmosphere.

The atmosphere in the round bottomed flask can be controlled by means of a Teflon inlet tube which enters through the side of the microwave cavity. This tube is connected on the outside to an inert gas supply and on the inside to the round bottomed flask. The port through which the inlet tube passes is similarly protected by a copper tube or 'choke' which must be in good electrical contact with the body of the oven. To prevent leakage a choke of diameter equal to one half wavelength, *i.e.* 6 cm, should be at least one wavelength, 12 cm, long. The apparatus can be confirmed safe using a hand held microwave leakage detector capable of measuring power levels greater than 1 mWcm^{-2}.

When a homogeneous reaction proceeds at the normal boiling point of the solvent then the rate of reaction should be identical independent of whether the energy was introduced into the system by microwave heating or conventional conductive effects. However, for a typical unimolecular reaction with an activation energy of 100 kJ mol^{-1} and a pre-exponential factor of 4×10^{10} mol^{-1} s^{-1} it is anticipated that 10 °C superheating over the conventional reflux temperature of 77 °C will lead to a decrease in reaction time (time to reach 90% completion) by a factor of *ca.* 2—3.

It is well established that the rapid heating effect associated with microwave heating can cause superheating of water to about 110 °C.[49] The water heats so quickly that convection to the top surface and subsequent vaporization are insufficient to dissipate the excess energy. Superheating effects can be magnified by the addition of ions, *e.g.* NaCl, to the water which greatly increase the

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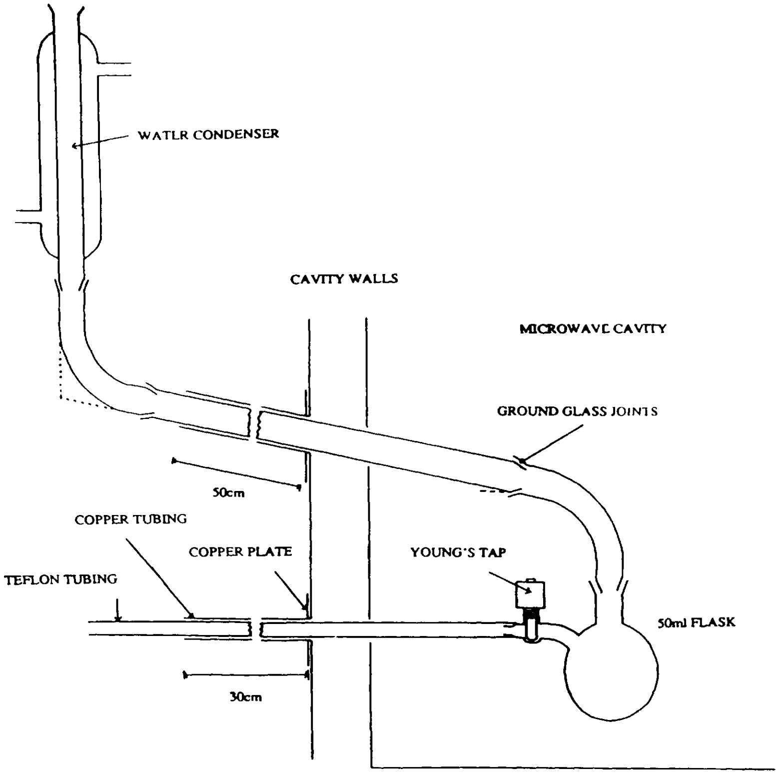
[48] D R Baghurst and D M P Mingos, *J Organomet Chem*, 1990, **384**, C57

[49] C R Buffler and T Lindstrom, *Microwave World*, 1988, **9**, 10



Modified microwave heating system applied.

Figure 16 *The microwave oven modified to allow studies under refluxing conditions*

conductive losses of the solution. Dramatic superheating effects have also been observed for water–oil mixtures where some interfacial polarization effects may be important.

Experiments with pure organic solvents have demonstrated that the reflux temperature is within 5 °C of the solvent boiling point. Whan[50] has studied the rates of organic esterification reactions, under comparable microwave and conventional conditions and has shown that the rates of reaction are identical under the two methods. Therefore there is no specific microwave effect and no superheating.

When the reaction conditions are not homogeneous or there are large quantities of mobile ions present then it is possible that localized superheating effects could lead to a small but significant increase in the reaction rate. There is

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[50] D. Whan, University of Hull, personal communication.

Table 5 *Microwave syntheses of organometallic compounds under reflux conditions*[48]

				Reaction times	
Reactants	*Product*	*Solvent*	*Yield (lit)*	*Microwave reflux*/min	*Conventional reflux*/h
$RuCl_3{\cdot}xH_2O$, PPh_3	$RuCl_2(PPh_3)_3$	MeOH	85(74)	30	3
$RuCl_3{\cdot}xH_2O$, cyclohexadiene	$[RuCl_2(\eta\text{-}C_6H_6)]_2$	EtOH	85(95)	30	4
$RuCl_3{\cdot}xH_2O$, α-phellandrene	$[RuCl_2(\eta\text{-cymene})]_2$	EtOH	67(65)	10	4
$RhCl_3{\cdot}xH_2O$, cyclooctadiene	$[RhCl(cod)]_2$	$EtOH/H_2O$ (5:1)	87(94)	25	18
$KReO_4$,PPh_3	$ReOCl_3(PPh_3)_2$	$EtOH/H_2O$	94(95)	30	5

some evidence, for example, that open vessel dissolution of geological and biological samples using acid solutions proceed at a faster rate in the microwave cavity than under conventional conditions.[51,52]

Table 5 provides some examples of organometallic syntheses which have been undertaken using the microwave reflux apparatus. The reported reaction times for these syntheses taken from the literature are also given in the Table. The total synthesis times have been reduced by a factor of 6—40 times. Prior to concluding that a specific microwave acceleration effect is in action it should be emphasized that literature reaction times have a large uncertainty built into them. Nonetheless, some useful decrease in reaction time is occurring whose origin has not been well established. Contributing factors may be:

(1) Some superheating effects due to the presence of large number of ions present.

(2) A more efficient and rapid achievement of the reaction temperature when microwave dielectric heating effects are used.

(3) More efficient mixing of reactants and some localized superheating effects on the boundary between non-miscible liquids and solutions. The Maxwell–Wagner component of the dielectric loss may be particularly important in this respect.

(iii) *Organic Synthesis at One Atmosphere.* Some induced selectivity arising from the use of microwaves is suggested by the recent studies of the Diels–Alder reaction of 6-demethoxy-β-dihydrothebaine with an excess of methyl vinyl ketone to yield the two adducts shown in Scheme 1.[53] When the reaction was performed under conventional conditions extensive polymerization of the dienophile resulted, which made the work-up and the isolation of the adducts

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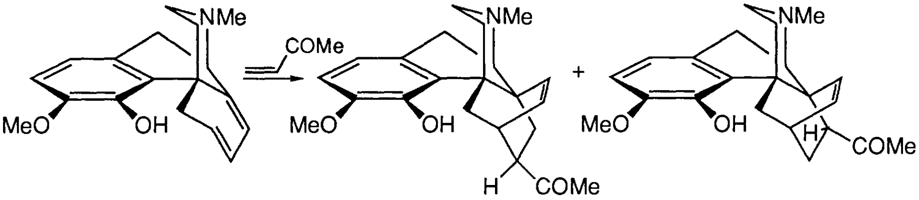
[51] K I Mahan, T A Foderaro, T L Garza, R M Martinez, G A Maroney, M R Trivisonno, and E M Willging, *Anal Chem*, 1987, **59**, 938

[52] P Aysola, P D Anderson, and C H Langford, *Anal Chem*, 1988, **21**, 2003

[53] J T M Linders, J P Kokje, M Overhand, T S Lie, and L Maat, *Recl Trav Chim Pays-Bas*, 1988, **107**, 449



Scheme 1

cumbersome. Using a modified microwave oven 6-demethoxy-β-dihydrothebaine was refluxed in methyl vinyl ketone. The reaction reached completion in 24 hours and substantially less polymeric material was formed.

B. High Pressure Conditions.—The effective coupling between microwaves and polar inorganic and organic solvents can be utilized to accelerate the rates of a reaction significantly if the reactants can be contained within a closed vessel which is transparent to microwaves and can sustain the high pressures induced. The rapid heating of only the solvents within the autoclave leads to significant advantages compared with high pressure steel autoclaves used with conventional heating processes. There are a number of plastic materials which are microwave transparent and can form the basis of pressure vessels, but it is also necessary for them to be chemically inert and sufficiently strong to accommodate the pressures induced. The temperatures and pressures generated in such an autoclave depend on the level of the input microwave power, the dielectric loss of the reacting solution, the volatility of the solvent, the volume of the container occupied by the solvent, and whether gases are generated in the reaction. Figure 17 illustrates the relationship between the temperature and pressure generated in a closed vessel for water and EtOH.[54] Clearly for reactions in aqueous solutions a pressure of *ca.* 5 atm. is generated at 150 °C, whereas for the more volatile EtOH a pressure of 12 atm. is generated at the same temperature. These parameters largely define the pressure requirements of the vessel although it should be emphasized that it is necessary also to have a pressure release valve incorporated into the device if this methodology is to be used routinely and safely.

Parr[55] have developed a range of acid digestion vessels which can accommodate pressures up to 80 atm. and temperatures up to 250 °C. These devices, an example of which is shown in Figure 18, were originally designed for the acid digestion of geological, botanical, metallurgical, and biological samples,[56] but can also be utilized for a range of inorganic and organic syntheses. The reactants are placed in a Teflon cup with a volume of *ca.* 23 cm^3 which is tightly sealed using an O-ring and cap, also made of Teflon. Teflon has the advantage of being chemically inert and therefore is a suitable containment vessel for acids and most

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[54] 'Chemical Engineers Handbook', ed. J. H. Perry, 3rd edn., McGraw-Hill, New York, 1950.

[55] Parr Instrument Company, Moline, Illinois 61265, USA.

[56] 'Introduction to Microwave Sample Preparation', ed. H. M. Kingston and L. B. Jassie, American Chemical Society, Washington, 1988.

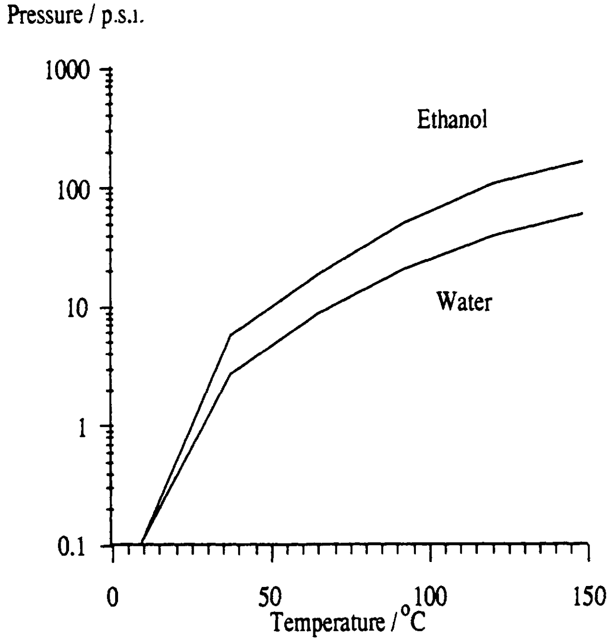

Figure 17 *Temperature versus pressure curves for* H_2O *and* EtOH [54] (1 atm = 14 7 psi)

commonly used organic and inorganic solvents It does, however, suffer two disadvantages—it has a tendency to flow and creep, particularly at temperatures above 150 °C, and it is slightly porous Therefore, repeated use of the vessel above 150 °C can lead to distortions which reduce the pressure limits of the vessel from its initial 80 atm The porosity leads to some incorporation of materials, particularly organic tars and metal powders, into the walls of the reaction vessel The Teflon cup is contained within a larger vessel made of polyetherimide The outer container has two sections which screw together Pressure release is controlled by a large rubber section which presses down on the lid of the Teflon cup When the pressure is developed within the vessel a screw rises from the top of the vessel Each 2 mm rise corresponds to around 10 atm pressure Excessive pressure is released on compression of the rubber section which leads to fracture of the O-ring and release of the reactants through venting holes

An alternative acid digestion system has been developed by CEM [57] and is shown in Figure 19 The advantage of this alternative system is that, while the maximum working pressure is restricted to 14—15 atm, the pressure can be continuously monitored by a transducer outside the oven The pressure is conveyed to the transducer *via* a thin Teflon tube which passes through a port in

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[57] CEM Corporation, Matthews, North Carolina 28106, USA

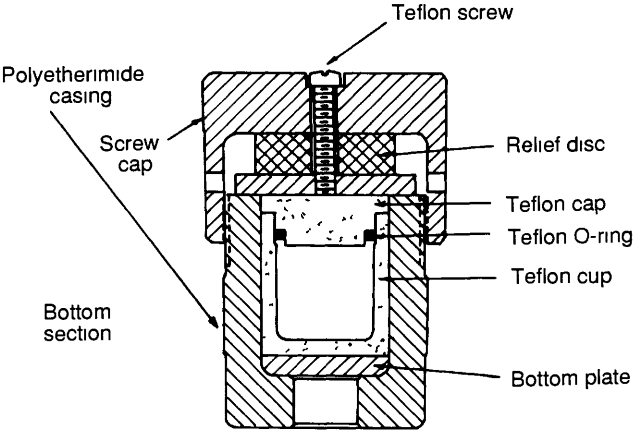

Figure 18 *Schematic illustration of the Parr acid digestion bomb*[55]

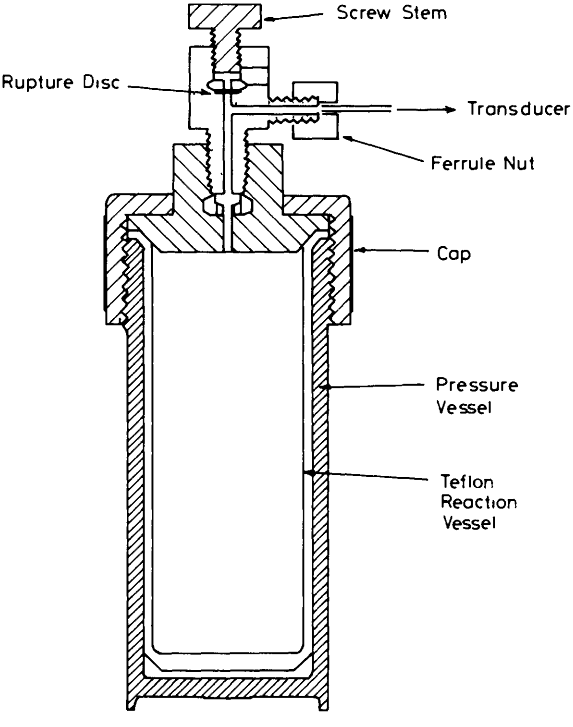

Figure 19 *Schematic illustration of the CEM acid digestion system*[57]

Table 6 *Relationship between temperature and time for a first order reaction*

T/°C	*Rate constant, k*/s^{1}	$t_{9/10}$
27	155×10^{7}	4126h
77	$4\ 76 \times 10^{5}$	13 4h
127	$3\ 49 \times 10^{3}$	11 4min
177	$9\ 86 \times 10^{2}$	23 4s
227	1 43	1 61 s

the side of the microwave oven A feedback system has been developed by CEM to allow constant pressures to be held in the vessels over extended periods Once again a pressure release mechanism is used to ensure pressure is kept below the specified maximum The vessel has a much larger volume which should allow larger quantities of inorganic and organic material to be processed than has previously been possible using the Parr autoclave

Both types of acid digestion apparatus have been used to shorten the time scales of a wide range of organic and inorganic reactions Prior to a discussion of specific applications it is instructive to provide some estimate of the magnitude of the acceleration rates predicted on the basis of elementary reaction kinetics theory

For a first order reaction which would require approximately 12—24 hours at 60—80 °C to produce a yield of *ca* 90% appropriate kinetic parameters are an activation energy, $E_a = 100$ kJ mol^{1} and a pre-exponential factor of $A = 4 \times 10^{10}$ mol^{-1} s^{-1} For these parameters the $t_{9/10}$ lifetimes (times for 90% completion) can be calculated for temperatures between 27 and 227 °C (see Table 6) Therefore, a reaction which commonly takes *ca* 13 4h to proceed to 90% completion in a solvent refluxing at 77 °C will achieve a comparable yield in 23 4s if undertaken in a closed vessel where the temperature is maintained at 177 °C A similar time reduction factor, *i e*, approximately 10^3, can be estimated for a second order reaction based on the same parameters

Therefore this microwave methodology has the following potential to introduce into a closed vessel which is transparent to microwaves energy sufficient to raise the temperature from ambient to *ca* 200 °C in less than a minute, and thereby cause the total reaction time to be reduced by *ca* 10^3 The introduction of energy so rapidly and effectively into a closed reaction vessel containing volatile organic compounds must take due regard of the likely pressure which is generated and the necessity of incorporating a safety device which allows any excess pressure to be released

Some examples of syntheses conducted under high pressure conditions are as follows

(i) *Organometallic Compounds* The rhodium(i) and iridium(i) dimers [M_2Cl_2(di-olefin)$_2$] (M = Rh or Ir) are widely used as starting materials for organometallic syntheses and are conventionally synthesized from $MCl_3 \cdot xH_2O$ and the olefin in aqueous alcohol Good yields are obtained after many hours of refluxing (4—36) of refluxing in alcohol–water mixtures Using the Parr autoclave described above, microwave radiation of 2 45 GHz and a power level of 500 W, these dimers can be

Table 7 *Organometallic syntheses in the Parr bomb*[58]

Product	*Reaction mixture*	*Reaction time*/s	*Yield*/%
$[Rh(C_8H_{12})Cl]_2$	$RhCl_3 \cdot xH_2O$, C_8H_{12}, $EtOH/H_2O$ (5:1)	50	91
$[Rh(C_7H_8)Cl]_2$	$RhCl_3 \cdot xH_2O$, C_7H_8, $EtOH/H_2O$ (5:1)	35	68
$[Ir(C_8H_{12})Cl]_2$	$IrCl_3 \cdot xH_2O$, C_8H_{12}, $EtOH/H_2O$ (5:1)	45	72
$[Rh(\eta\text{-}C_5H_5)_2]PF_6$*	$RhCl_3 \cdot xH_2O$, C_5H_6, MeOH	30	62

* Methanolic NH_4PF_6 added to the reaction product to obtain the yellow salt

conveniently synthesized from the same reagents in good yields in less than one minute.[58] In the reactions 0.2—1.0g of the platinum metal salts were used and the total reaction volumes were approximately $15\,cm^3$.

The range of compounds that can be synthesized in this manner, their yields, reaction mixtures and reaction times are summarized in Table 7.[58] The maximum temperatures achieved in these reactions correspond approximately to 170 °C. With some olefins, *e.g.* cyclo-octene and cyclo-octatetraene, the dimeric complexes were not isolated and rhodium metal was the major product. In these cases the final products are unstable above 160 °C and presumably are formed and subsequently decomposed.

The same procedures were used to synthesize $[RuCl_2(\eta\text{-}C_6H_6)]_2$ from $RuCl_3 \cdot xH_2O$ and 1,3-cyclohexadiene in aqueous ethanol. A reaction time of 35 s gave a yield of 89%. Interestingly, when $RhCl_3 \cdot xH_2O$ was reacted with freshly distilled cyclopentadiene and exposed to microwaves for 30s the product was the sandwich cation $[Rh(\eta\text{-}C_5H_5)_2]^+$, which was isolated as the PF_6^- salt, rather than the dimer produced conventionally. This compound is usually synthesized using the Grignard reagent C_5H_5MgBr rather than directly from cyclo-pentadiene.

Using a different type of Teflon autoclave vessel various post transition metal organometallic compounds have been synthesized.[59] In the 100 cm^3 Savillex[60] Teflon bottle, with screw cap, a maximum solvent volume of 12 cm^3 was used to perform the reactions shown in Table 8. The disadvantage of this type of vessel is that there is no pressure indication present and no safety pressure release mechanism.

In the examples of metallation of aromatic rings, ligand redistribution reactions and reactions of metallo-organic species such as $Al(OPr^i)_3$ a great reduction in reaction time has been found. It was noticed that the yields were generally of the same order as the conventional syntheses and where the separation of the products is difficult no particular advantage was evident from the microwave technique in terms of isolation.

(ii) *Co-ordination Compounds.* A wide range of co-ordination compounds of substitutionally inert transition metal ions have been rapdily and conveniently

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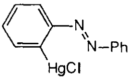
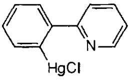
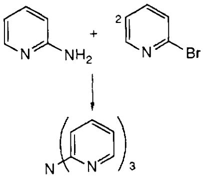
[58] D. R. Baghurst, D. M. P. Mingos, and M. J. Watson, *J. Organomet. Chem.*, 1989, **368**, C43.

[59] M. Ali, S. P. Bond, S. A. Mbogo, W. R. McWhinnie, and P. M. Watts, *J. Organomet. Chem.*, 1989, **371**, 11.

[60] Savillex Corporation, Minnetoka, Minnesota 55345, USA.

Table 8 *Summary of results of microwave heating*[59]

Reaction	*Solvent*	*Microwave oven*		*Conventional method*	
		Time/ min	*Yield/* %	*Time/* h	*Yield/* %
Preparation[a] of 	EtOH	30	33	22	40
Preparation[a] of 	EtOH	47	29	24	36
$Ph_3Bi + 3BiCl_3 \rightleftharpoons 3PhBiCl_2$[b]	Propanol	6	46	3—4	30—68
$3Ph_4Sn + 2BiCl_3 \longrightarrow Ph_3Bi + Ph_2SnCl_2$	EtOH Toluene	6		n/a	
	EtOH	6	20	16	15
$Al(OPr^{i})_3 + HOCH_2CH(OH)CH_3$[e]	none	6	mixed	4—6	mixed

[a] $Hg(OOCH_3)_2$ used in microwave experiment Conversion to chloro-derivative *via* LiCl [b] Isolated as 2,2′-bipyridyl complex [c] Mixture of products, difficult to separate

synthesized using microwave dielectric loss heating effects.[61] The synthesis of co-ordination compounds of substitutionally inert transition metal ions, and particularl d^3, d^8, and low spin d^6 ions, can lead to long and tedious synthetic procedures. This is particularly true for second and third row transition metals with these electronic configurations which are exceptionally inert.

The co-ordination complexes summarized in Table 9 represent a range of syntheses requiring from a minimum of 2 hours, *e.g.* $[IrCl_3(9S3)]$, to one week for $[RuCl(CO)(bpy)_2]Cl$ under conventional conditions. Using the Parr autoclave the co-ordination compounds listed have been synthesized in good yields in a matter of minutes with 500—650 W power levels. In some cases the pressure limitations of the vessel did not allow the whole reaction to be completed in one step and it was necessary to allow the reaction mixture to cool for approximately 15—20 minutes before subsequent exposures of microwaves each of 30 s duration were applied.

The synthesis of the crown thioether complex $[IrCl_3(9S3)]$ required only 16 s

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[61] D R Baghurst, S R Cooper, D L Greene, D M P Mingos, and S M Reynolds, *Polyhedron*, 1990, **9**, 893

Table 9 *Co-ordination complexes synthesized by microwave techniques*[61]

			Yield/ %	*Reaction time*	
Product	*Reactants*	*Solvent*		*Microwave*/s	*Conventional*/h
Cr(dpm)$_3$	$CrCl_3 \cdot 3H_2O$, urea, dipivaloylmethane	EtOH/H_2O	71	40	24
IrCl(CO)(PPh$_3$)$_2$*	$IrCl_3 \cdot xH_2O$, PPh_3	DMF	70	45	12
IrCl$_3$(9S3)	$IrCl_3 \cdot xH_2O$, 9S3	MeOH	98	16	2
[PtCl(tpy)]Cl·3H$_2$O	K_2PtCl_4, tpy	H_2O	47	2 × 30	24—100
[AuCl(tpy)]Cl·3H$_2$O	$HAuCl_4$, tpy	H_2O	37	2 × 30	24
[RuCl(CO)(bpy)$_2$]Cl	$RuCl_3 \cdot xH_2O$	DMF	70	3 × 20	168
[Ru(9S3)$_2$](PF$_6$)$_2$	$RuCl_3 \cdot xH_2O$, 9S3	MeOH	49	6 × 25	n/a

dpm = 2,2,6,6-tetramethyl-3,5-heptadionato; 9S3 = 1,4,7-trithiacyclononane; tpy = 2,2′,2″-terpyridine; bpy = 2,2′-dipyridyl; DMF = dimethylformamide

* The reaction product was at times contaminated with [IrCl$_3$(CO)(PPh$_3$)$_2$] which was reduced to [IrCl(CO)(PPh$_3$)$_2$] with zinc in DMF

for a virtually quantitative yield, compared to 3 h in refluxing methanol using conventional techniques. The synthesis of the related ruthenium complex [Ru(9S3)$_2$](PF$_6$)$_2$ by conventional techniques required the prior conversion of $RuCl_3 \cdot xH_2O$ into the labile intermediate Ru(SO$_3$CF$_3$)$_3$ or [Ru(dmso)$_6$]$^{2+}$. Using the microwave technique it was synthesized directly from $RuCl_3 \cdot xH_2O$ and required a total of 150 s microwave exposure (6 times 25 s) and gave the product in 49% yield.

The terpyridine complexes of $\mathrm{Pt^{II}}$ and $\mathrm{Au^{III}}$ listed have been extensively studied as metallo-intercalation reagents for DNA. Both compounds were obtained in good yield using H_2O as the solvent. The synthesis of the gold compound resulted in the formation as a byproduct of the complex salt [Au(terpy)Cl]$_2$[AuCl$_2$]$_3$[AuCl$_4$] which had been previously characterized.

The pentadionato- complex listed in Table 9 provides an example of a substitutionally inert first row transition metal complex made by the microwave technique. It has been widely used as a spin lattice relaxation reagent in NMR. In the synthesis of [IrCl(CO)(PPh$_3$)$_2$] and [RuCl$_2$(CO)(bpy)$_2$]Cl the high dielectric loss solvent DMF was used. In these reactions DMF also acts as the source of the carbonyl ligands.

Polypyridyl complexes of $\mathrm{Ru^{II}}$ have been the subject of widespread interest in recent years because of their unique photochemical and redox properties. The syntheses of these complexes are often time consuming and require several steps. For example, the recently reported synthesis of [Ru(bpy)$_3$](PF$_6$)$_2$ required the initial conversion of $RuCl_3 \cdot xH_2O$ into [RuCl$_2$(CO)$_2$]$_n$ by refluxing in methanoic acid followed by the substitution of the carbonyl ligands by bpy using Me$_3$NO in refluxing 2-methoxyethanol. It has been demonstrated that microwave dielectric loss heating effects can provide a general and convenient synthetic method for the polypyridyl complexes of ruthenium(II),[62] summarized in Table 10. It is

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[62] D. L. Greene and D. M. P. Mingos, *Transition Metal Chem.*, 1991, **16**, 71.

Table 10 *Microwave syntheses of* Ru^{II} *polypyridyl complexes*[62]

Compound	*Wash sequence*	*Yield/%*	*Microwave exposures*
$[Ru(bpy)_3](PF_6)_2$	3 × 5 cm^3 Et_2O	68	2 × 20
$[Ru(tpy)_2](PF_6)_2$	3 × 5 cm^3 MeOH, 2 × 5 cm^3 Et_2O	60	2 × 20
$[Ru(phen)_3](PF_6)_2$	1 × 5 cm^3 MeOH, 3 × 5 cm^3 Et_2O	74	2 × 20
$[Ru(bpy^*)_3](PF_6)_2$	10 cm^3 $MeOH/H_2O$ (1:1), 2 × 5 cm^3 Et_2O	94	2 × 20

bpy = 2,2′-dipyridyl, tpy = 2,2′,2′-terpyridyl, phen = 1,10-phenanthroline, bpy* = 4,4′-di-t-butyl-2,2′-dipyridyl

remarkable that yields of 60—94% were achieved using only 40 s of microwave radiation at a power level of 650 W.

Microwave techniques have recently been used in the synthesis of metal–metal bonded compounds. The preparation of $[Mo_2(acetate)_4]$ takes between 12 and 48 hours by conventional techniques and proved to be a challenge even using microwaves. The Parr autoclave containing the reactants was exposed to 325 W of 2.45 GHz microwave power for 15 minutes to obtain molybdenum acetate dimer in 75% yield:[63]

$$Mo(CO)_6 \xrightarrow{CH_3CO_2H\ +\ \text{anhydride}} Mo_2(O_2CCH_3)_4$$

(iii) *Organic Syntheses.* Early work in this area was performed by Gedye[31,64,65] and Giguerre.[66,67] In the former case a variety of reactions were studied and progress has been made on defining the important experimental variables. The reactions which were performed in 150 cm^3 Savillex screw cap Teflon bottles are illustrated in Table 11. Giguerre and co-workers used 10 cm^3 sealed tubes or 15 cm^3 screw cap vials. Estimates of the reaction temperatures were obtained by using sealed capillaries containing organic compounds of known melting points either sealed within or affixed to the side of the reaction container. The results appear in Table 12. Care was taken to optimize conventional reaction conditions before comparisons were made with microwave syntheses.

Both groups suggest that the rate of heating of the solvent depends qualitatively upon the room temperature dielectric constant although as we stressed in Section 3 the dielectric loss is the more reliable parameter. Gedye[31] has also shown that the rate of acceleration relative to conventional syntheses depends upon container volume, the ratio of reaction volume to container

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[63] D L Greene, unpublished results

[64] R Gedye, F Smith, K Westaway, H Ali, L Baldenisa, L Laberge, and J Rousell, *Tetrahedron Lett*, 1986, **27**, 279

[65] R N Gedye, F E Smith, and K C Westaway, *Educ Chem*, 1988, **25**, 55

[66] R J Giguerre, T L Bray, S N Duncan, and G Majetich, *Tetrahedron Lett*, 1986, **28**, 4945

[67] R J Giguerre, A M Namen, B O Lopez, A Arepally, D A Ramos, G Majetich, and J Defauw, *Tetrahedron Lett*, 1987, **28**, 6553

Table 11 *Results obtained with a* 720 W, 2.45 GHz *microwave oven*

Synthesis	*Microwave*	*Classical*	$\frac{\textit{Rate (microwave)}}{\textit{Rate (classical)}}$
Hydrolysis of benzamide to benzoic acid	10 min, 99%	1 h, 90%	6
Oxidation of toluene to benzoic acid	5 min, 40%	25 min, 40%	5
Esterification of benzoic acid with methanol	5 min, 76%	8 h, 74%	96
Esterification of benzoic acid with propanol	18 min, 86%	7.5 h, 89%	25
Esterification of benzoic acid with *n*-butanol	7.5 min, 79%	1 h, 82%	8
S_N2 reaction of 4-cyanophenoxide ion with benzyl chloride	3 min, 74%	12 h, 72%	240
	4 min, 93%	16 h, 89%	240

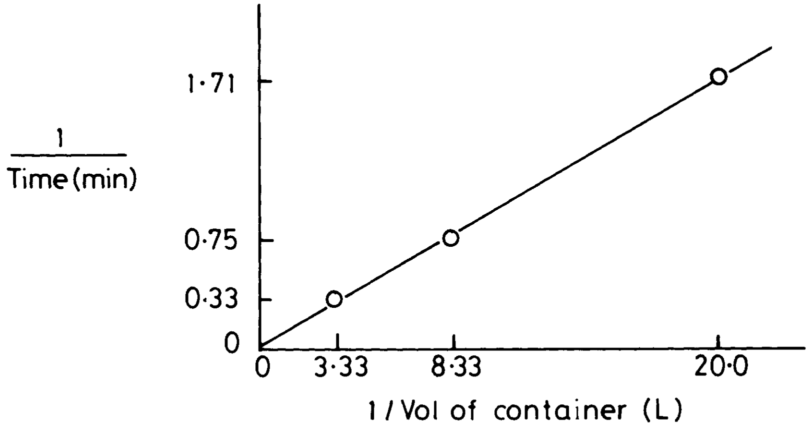
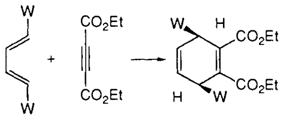
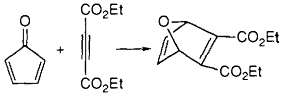
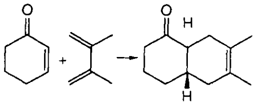
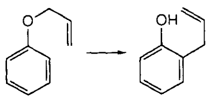
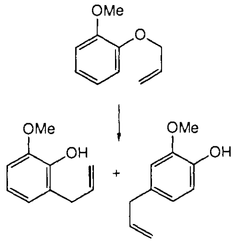
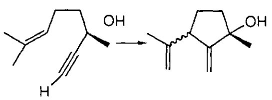


Figure 20 *Effect of reaction vessel volume on the rate of formation of benzyl-*1*-cyanophenyl ether*[31]

volume, and the solvent boiling point. Thus lower boiling solvents give reactions where the greatest rates of acceleration are observed. The inverse relationship between reaction flask volume and acceleration was estimated by the time required to obtain 65% yield of benzyl-4-cyanophenyl ether (Figure 20). These results suggest that the rate of reaction increases as the pressure increases. The effect of the ratio of the reaction volume to vessel volume is more complex. When the reaction volume is small the pressure and hence the reaction rate increases as the volume of the solvent in the reaction vessel increases. However, a point is reached where this increase is no longer observed since it takes longer to heat a large volume of solvent to the same temperature using the available microwave power.

Using this information Gedye[31] has increased the rate of acceleration observed in the esterification of benzoic acid in 1-propanol. The rate enhancement

Table 12 *Microwave acceleration of Diels–Alder Claisen and ene reactions*

Reaction	*Microwave*	*Literature*	*Control*
	12 min neat, 55% 325° < 361 °C	5 h neat, 67% 150 °C	5 h neat, 81% 150 °C
	10 min neat, 66% 325° < 361 °C	4 h neat, 95% 100 °C	4 h neat, 68% 100 °C
	15 min neat, 25% 400° < 425 °C	72 h neat, 20% 200 °C	(a) 3 days neat, 89% 195 °C (b) 2 h neat, 75% 195 °C
	(a) 10 min neat, 21% 325° < 361 °C (b) 6 min DMF, 92% 325° < 361 °C	6 h neat, 85% 240 °C	6 min neat, 17% 320 °C
	(a) 12 min neat, 71% 370° < 361 °C (b) 5 min DMF, 72% 300° < 315 °C (c) 90 s n-methyl formamide 87%, 276° < 300 °C	85 min neat, 85% 240 °C	(a) 45 min neat, 71% 265 °C (b) 12 min neat, 92% 320 °C
	15 min neat, 62% 400° < 425 °C	12 h neat, 85% 180 °C	12 h neat, 60% 180 °C

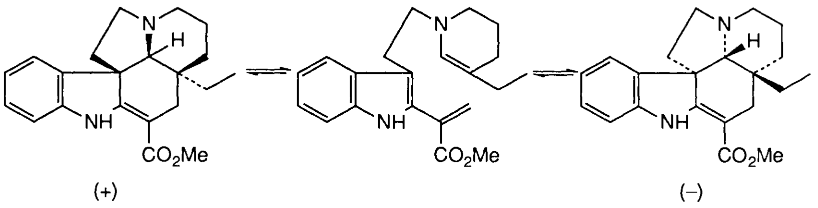
was increased from 18 to 60 when the volume of the reaction mixture was altered to maximize the heating effect Further rate enhancement to 180 times conventional was achieved by increasing the available microwave power from 560 to 630 W

Practical application of these microwave techniques has now spread to the fields of natural product racemization and the formation of radiochemicals

Table 13 *Fluorination yields (%) for the aromatic substitution reaction*[69]

$$18F^- + p\text{-X-C}_6H_4\text{-G} \longrightarrow p\text{-}^{18}F\text{-C}_6H_4\text{-G} + X^-$$

X	G	*Microwave/* 5 min	135 °C 5 min	135 °C 30 min
NO_2	CN	68 ± 5	52 ± 2	82 ± 2
NO_2	COMe	25 ± 3	10 ± 5	22 ± 1
NO_2	$CO(CH_2)_2CH_2$	77 + 5	24 ± 7	80 ± 1
F	COMe	70 ± 1	12 ± 2	73 ± 2



Scheme 2

Using sealed tubes small quantities of the natural product (−)-vincadifformine has been racemized to the synthetically more useful (+)-vincadifformine (Scheme 2).[68]

The optically active alkaloid is racemized through the intervention of a secodine intermediate by concurrent Diels–Alder cycloreversion and cycloaddition. In the microwave racemization a degassed solution of (−)-vincadifformine in DMF was sealed in a glass tube under argon and heated for 20 minutes in a 500 W microwave oven. The (+)-enantiomer serves as the synthetic precursor of the Eburnane alkaloid, (+)-vincamine, which has been found to be a useful remedy in the treatment of cerebral insufficiency.

The rapid and high yield synthesis of radiopharmaceuticals labelled with short-lived radionuclides remains an important challenge to the synthetic chemist. With the positron emitting nuclides ^{122}I ($t_{\frac{1}{2}}$ 3.6 min), ^{11}C ($t_{\frac{1}{2}}$ 20 min), and ^{18}F ($t_{\frac{1}{2}}$ 110 min) this is particularly so. Using 3 cm^3 Reacti-vials and a 500 W microwave oven the nucleophilic reactions of activated nitrobenzenes with ^{18}F-fluoride, and isotope exchange reactions of activated and deactivated halogenoarenes using ^{18}F-fluoride and ^{131}I-iodide have been studied.[69] The microwave syntheses are much faster than comparable thermal syntheses (see Table 13). The shorter microwave treatment relative to conventional heating not only leads to less decay of the radio-labelled product, but may also cause less degradation of the reagents and the generation of side-products which make isolation of the desired labelled compound difficult.

Isotope exchange of ^{131}I-iodide reached completion within 5 minutes in

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[68] S. Takano, A. Kijima, T. Sugihara, S. Satah, and K. Ogasawara, *Chem. Lett.*, 1989, 87.

[69] D. R. Hwang, S. M. Moerlein, L. Lang, and M. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1987, 1799.

Table 14 *Zeolite syntheses under microwave conditions*[73]

Zeolite	*Formula*	*Microwave power*/Watts	*Time*/min
Na zeolite A	$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot 27H_2O$	300	45 in pulses
Faujasite	$Na_2[Al_2Si_5O_{14}]\cdot 10H_2O$	600	3
Analcime	$Na_{16}[(AlO_2)_{16}(SiO_2)_{32}]\cdot 16H_2O$	600	>3
Hydroxy-sodalite	$Na_8[AlSiO_4](OH)_2\cdot 6—8H_2O$	600	2 5

substrates both activated and deactivated towards nucleophilic substitution. Aromatic iodination yields in excess of 80% were obtained within 60s, indicating the utility of this synthetic technique for reactions with positron-emitting ^{122}I ($t_{\frac{1}{2}}$ 3.6 min) and γ-emitting ^{123}I ($t_{\frac{1}{2}}$ 13.2 h).

As noted by Gedye, large scaling up of organic reactions in a microwave oven is not feasible using larger Teflon vessels since more microwave power is needed to process larger volumes. Instead techniques have been devised involving pumping the reactants from a reservoir through a reaction coil inside a microwave oven and on through the walls to a collection vessel. CSIRO, in Australia, have developed a continuous flow apparatus which at present can process materials at a rate of 20 cm^3 per minute.[70] It is envisaged that their reactor will be able to process 4 litres of material a minute over many hours at temperatures up to 200 °C and pressures up to 12 atm. Recently Chen[71] has developed a similar reactor allowing more than 20 g of material to be processed. The effects of irradiation time, power level, and reaction quantity were compared with closed vessel microwave techniques. Generally the reaction conversion efficiency in the continuous flow system exceeded that found in a closed environment.

(iv) *Zeolites.* The synthesis of zeolites by microwave radiation is the subject of a recent patent.[72] A range of zeolites have also been synthesized using a 650 W microwave oven and a Parr autoclave.[73] The long exposure times to microwave radiation quoted in Table 14, particularly in the synthesis of Na zeolite A, mean that the autoclave is operating near its maximum temperature capability. The samples are highly uniform with particle sizes >2 μm. Under high power levels the more condensed sodalite structure tends to be obtained due to the higher pressures and temperatures involved. Some differences in sample morphology have been noted when conventional and microwave products are compared.

Additionally, zeolite exchange reactions have been performed. Replacement of Na^+ ions by Co^{2+} ions in faujasite shows comparable degrees of substitution using either one hour of conventional heating or 60 s microwave heating. The *X*-

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[70] C Peterson, *New Scientist*, 9th September 1989, **123**, 44

[71] S -T Chen, S -H Chiou, and K -T Wang, *J Chem Soc*, *Chem Commun*, 1990, 807

[72] V C Vartuli, P Chu, and F G Dwyer, 'Crystallisation Method Using Microwave Radiation', US Patent Application 4,778,666, 1988

[73] R H I Gill and D M P Mingos, unpublished results

Table 15 *Comparison of syntheses of* $VO(PO_4){\cdot}2H_2O$ *intercalates using microwave and conventional thermal techniques*[75]

	Microwave syntheses		*Conventional syntheses*		*Lattice expansions*[b]	
Conditions:[a] *Guest*	t/min	*Stoichiometry*	t/h	*Stoichiometry*	c/Å	Δ/Å
Pyridine	5	0.84	36	0.35	9.55	5.44
4-Methylpyridine	3	0.86	12	0.60	10.56	6.45
4-Phenylpyridine	2 × 5	0.85	64	0.51	12.23	8.12[c]

[a] Host: $VO(PO_4){\cdot}2H_2O$. [b] Co-ordinated water is lost during the reaction of $VOPO_4{\cdot}2H_2O$ (c = 7.41 Å). Δc represents the difference in the length of the c axis for the intercalation compound and that of anhydrous $VOPO_4$. [c] Another phase is also observed with a layer expansion of 9.89 Å.

ray powder patterns are identical. In the case of Co^{2+} exchange for Na^+ in sodalite, complete replacement was possible in just 4.5 min of microwave heating.

(v) *Intercalation Compounds.* The intercalation of organic and organometallic compounds into layered oxide and sulphide structures has attracted considerable interest in recent years. The kinetics of the intercalation processes are often slow and consequently even after refluxing for several days these reactions do not always proceed to completion. Ultrasound has been shown to increase the rates of intercalation reactions but, as with the thermal methods, can result in loss of crystallinity of the samples. This makes structural characterization of the intercalated compounds using *X*-ray powder techniques problematical.[74]

Using a Parr digestion bomb several pyridine intercalates of the layered mixed oxide α-$VO(PO_4)$ have been prepared.[75] In a typical experiment α-$VO(PO_4)$ and the pyridine (or an equivalent volume of pyridine in xylene) were placed in the Teflon autoclave and exposed to 650 W of 2.45 GHz microwave radiation for several minutes. The length of each microwave exposure was limited to *ca.* 5 minutes by the pressure limitations of the autoclave. The maximum temperature reached was 200 °C. Table 15 summarizes the results of the microwave experiments, together with the results of comparable control reactions which were carried out using conventional thermal techniques. The latter were performed in glass ampoules, where 100% intercalation corresponds to a stoichiometry of $VO(PO_4){\cdot}py_{0.85}$. Note that dramatic rate enhancements of the order 10^2—10^3 were generally observed.

An addition advantage of the microwave technique is the quality of the *X*-ray powder data obtained from the more crystalline microwave products. In Figure 21 the *X*-ray powder clearly shows the presence of two tetragonal phases. This is not apparent in the lower quality data from the conventional product.

Blank experiments have established that while α-$VO(PO_4){\cdot}2H_2O$ itself does

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[74] K. S. Suslick, *Science*, 1990, **247**, 1439.

[75] K. Chatakondu, M. L. H. Green, D. M. P. Mingos, and S. M. Reynolds, *J. Chem. Soc., Chem. Commun.*, 1989, 1515.

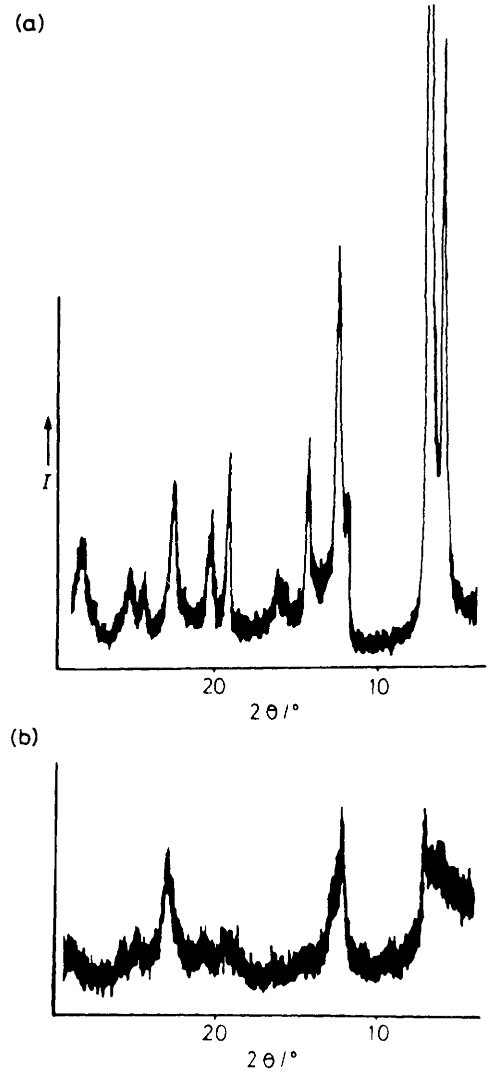

Figure 21 *A comparison of the X-ray powder diffraction patterns for the intercalation compounds of* α-$VO(PO_4)$ *with 4-phenylpyridine (a) microwave product and (b) conventional thermal product*

not strongly absorb microwaves, the intercalated products do Therefore, in the initial stages of the reaction the high temperature rise associated with the solution is primarily responsible for the rate enhancement These efficient heating effects rapidly lead to pressures of *ca* 50 atm and temperatures of 200 °C within a minute. In the latter stages of the reactions autocatalytic effects associated with the absorption of microwaves by the product may contribute to the completion of the intercalation reactions. These autocatalytic effects would have no analogues in conventional conductive heating.

6 Reactions Utilizing the Microwave Dielectric Loss Properties of Solids

From Table 3 in Section 3 it is apparent that many solids absorb microwaves and can be heated very rapidly to high temperatures. This opens up the possibility of using the coupling to microwaves of one component in a mixture to drive a solid state chemical reaction with a second component which may be transparent to microwaves.

A. Chemistry of Ceramic Processing.—The use of microwaves to process and sinter ceramics is thought to have the following advantages over classical heating:[76]

(i) *Reduced Cracking and Thermal Stress.* In microwave processing heat is generated inside the component while in furnace heating, by contrast, heat is absorbed from the outside and can lead to thermal stresses, cracking and other problems. Hence, microwave heating can be especially useful for densifying ceramic components.

(ii) *Economy.* Internal heating may turn out to be more economical since the oven itself is not heated.

(iii) *Increased Strength.* As a result of rapid heating by microwaves, the extent of non-isothermal processes such as segregation of impurities to the grain boundaries are minimized. Since sintering time is often reduced also, the possibility for secondary recrystallization (exaggerated grain growth) may be reduced. By minimizing impurity segregation, decreasing grain size and increasing sintered density, the mechanical properties of the ceramic are strengthened.

(iv) *Reduced Contamination.* The heating of the ceramic sample from the centre using microwaves limits the extent of contamination from the walls of the containment vessel.

The application of microwave energy in the field of ceramic processing and joining have been recently reviewed.[77–79] and we shall restrict ourselves to those results having chemical significance.

The overall rate of a chemical reaction is governed by the speed of the slowest step or steps. For many solid state reactions this slowest step is the diffusion of the reactants towards one another through an unreactive medium. Any process which can increase the bulk diffusion coefficient could lead to a dramatic enhancement in the rate of reaction. Much of the work on the microwave processing of ceramic composite materials suggests that enhanced transport

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[76] R. Dagani, *Chem. Eng. News*, 1988, **66**, 7.

[77] W. H. Sutton, *Am. Ceram. Soc. Bull.*, 1989, **68**, 376.

[78] D. Palaith and R. Silberglitt, *Am. Ceram. Soc. Bull.*, 1989, **68**, 1601.

[79] 'MRS Symposium Proceedings', ed. W. H. Sutton, M. H. Brooks, and I. J. Chabinsky, 1988, **124**.

properties occur when dielectric heating effects are applied The diffusion of various cations in Pyrex glasses and of ethylene oxide (EO) in polyvinylchloride (PVC) have been studied by both conventional and microwave heating

Cation diffusion in solid right circular cylinders of Pyrex glasses has been studied by back scattered electron microscopy profiling[80] Each cylinder was placed in a 50 cm^3 Pyrex crucible and was packed with either CoO (conventional case) or a concentrated solution of $Co(NO_3)2{\cdot}6H_2O$ (microwave case) Diffusion occurred to a depth of 40 mm in a sample heated conventionally to 925 °C for 60 minutes However, using microwave heating for just 15 minutes at a maximum temperature of 750 °C the diffusion depth was found to be 70 mm Additionally several cobalt-rich phases had developed in the microwave heated sample which were absent in the conventional sample Microwave processing at 1035 °C for just 10 5 minutes gave a diffusion length of 200 mm

Microwave radiation (2 45 GHz) has been shown greatly to accelerate the diffusion of EO in polymeric materials compared to conventional heating at the same temperature[81] Specifically the mode of action of the microwaves was studied by examining the desorption of EO from PVC Samples of PVC were saturated with EO in a controlled humidity apparatus prior to being heated by conventional and microwave heating The concentration of EO remaining in the PVC as a function of time was routinely determined by heating in an enclosed vial followed by analysis by chromatography The diffusion coefficient was found to be dependent upon the diffusant concentration which suggested that some interaction between EO and PVC was taking place

Values of the activation energy for diffusion were obtained from Arrhenius plots of the logarithm of diffusion coefficient *versus* inverse temperature for both conventional and microwave-enhanced diffusion, and there was a significant reduction in activation energy for the latter as shown in Figure 22 There is agreement, to within the range of experimental error, between this value and an energy equal to the activation energy for conventional diffusion less the translational kinetic energy of the diffusant molecules Therefore, it seems likely that the enhancement of the rate of diffusion of EO in PVC using microwaves is brought about by the active disruption of the EO/PVC hydrogen bonding resulting in a significant reduction in the proportion of immobilized diffusant molecules at any instant This suggests that the process could be generally applicable for enhancing diffusion for polar/polarizable materials when a proportion of the diffusant molecules are immobilized in the host material

B. Solid State Synthesis.—Where one or more of the components of a solid state reaction mixture absorbs microwaves strongly the heat so produced can be used to drive the reaction In Table 16 a range of syntheses achieved in this way are indicated[82] [83] Thus the strong absorption of V_2O_5 has been used to synthesize a

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[80] T T Meek R D Blake J D Katz J R Bradbury and M H Brooks *J Mat Sci Lett* 1988 7 928

[81] C Gibson I Matthews and A Samuel *J Microwave Power Electromag Energy* 1988 **23** 17

[82] D R Baghurst A M Chippindale and D M P Mingos *Nature* 1988 **332** 311

[83] D R Baghurst and D M P Mingos *J Chem Soc Chem Commun* 1988 829

Table 16 *Microwave solid state syntheses*[82,83]

Product	*Starting materials*	*Microwave synthesis* (min)	*Conventional synthesis* (h)
KVO_3	K_2CO_3, V_2O_5	7	12
$CuFe_2O_4$	CuO, Fe_2O_3	30	23
$BaWO_4$	BaO, WO_3	30	2
$La_{1.85}Sr_{0.15}CuO_4$	La_2O_3, $SrCO_3$, CuO	35	12
$YBa_2Cu_3O_{7-x}$	Y_2O_3, $Ba(NO_3)_2$, CuO	70	24

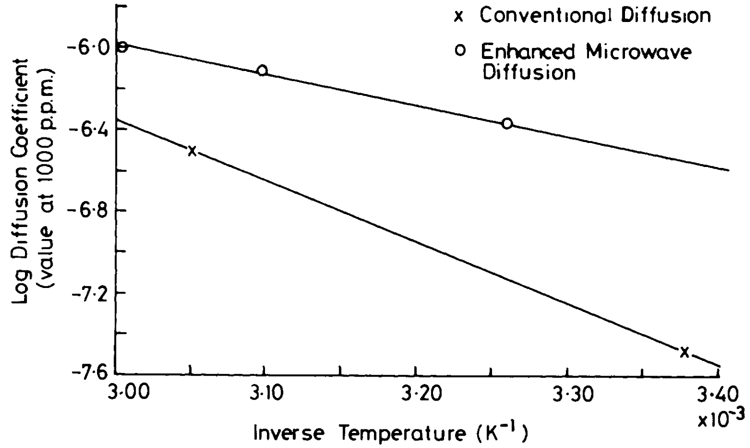

Figure 22 *Arrhenius plots for conventional and enhanced desorption*[81]

sample of KVO_3 from V_2O_5 and KCO_3. The starting materials are intimately mixed and can be pelletized, prior to being placed in alumina, zirconia, or silica crucibles, as appropriate. The crucible is placed on a firebrick to protect the cavity from the high temperatures reached.

Reaction times are shorter than those required conventionally to produce samples having comparable *X*-ray powder patterns. Thus, the samples appear to retain a high degree of crystallinity, and impurities and starting materials are absent from the final products. Recently the kinetics of product formation have been studied by calibrated *X*-ray powder techniques for microwave and thermal samples of $Sr_2LaFe_3O_{8+y}$. Using KCl as the internal standard a homogeneous microwave product was obtained after 36 minutes heating with around 500 W of microwave power. The sample temperature was measured at 1100 °C by a grounded, sheathed thermocouple. The temperature is believed to be reliable since higher temperatures (1200 °C and higher) would be expected to produce an orthorhombic rather than a cubic *X*-ray pattern. A comparable thermal sample was synthesized in 26 hours.

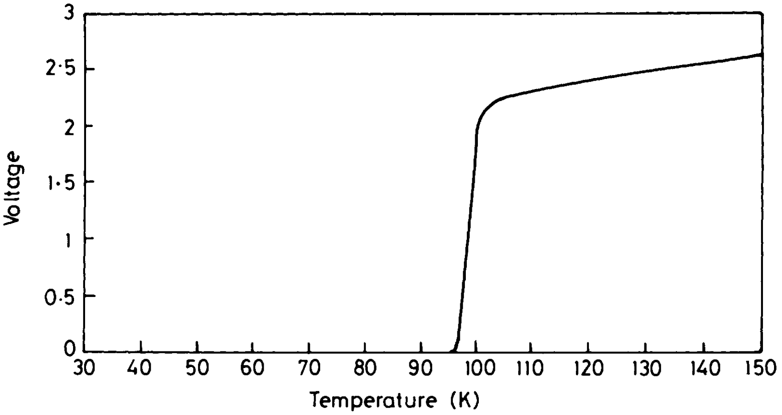

Figure 23 *Resistivity plot for a sample of* $YBa_2Cu_3O_{7-x}$ *synthesized by microwave techniques*

Several groups have synthesized samples of superconducting $YBa_2Cu_3O_{7-x}$ utilizing the coupling of CuO to microwaves in starting reaction mixtures and eventually the product itself.[82–84] It has been found that since the reacton time is much shorter than that required conventionally there is no need to slow cool the product in an oxygen atmosphere to obtain the orthorhombic superconducting phase. In Figure 23 the resistivity plot is shown for a typical sample synthesized from a stoichiometric mixture of CuO, $Ba(NO_3)_2$, and Y_2O_3. The sample was made in a 500 W domestic microwave oven which had been modified to allow the safe removal of the various nitrogen oxides under flowing oxygen. The high onset temperature for superconductivity of 96.5 K and the narrow nature of the transition to zero resistivity are comparable to those of samples produced under conventional conditions.

SEM studies on a sample of $YBa_2Cu_3O_{7-x}$[84] which had been synthesized conventionally but annealed in a microwave oven have shown encouraging results. The sintering occurs evenly resulting in smaller grains and lower sample porosity.

C. Decomposition Reactions.—The rapid heating of solids by microwaves provides an alternative to conventional pyrolysis procedures. Early studies showed that the products obtained by microwave heating of cellulose were similar to those obtained thermally but the time taken to reach reaction temperature and reaction times themselves were reduced significantly.[85] More recently the formation of 1,6-anhydro-β-D-glucopyranose, a useful chiral synthon, from starch or other 1 ⟶ 4 glucans has been studied.[86]

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[84] I Ahmad, G T Chandler, and D E Clark, in 'MRS Symposium Proceedings', ed W H Sutton, M H Brooks, and I J Chabinsky, 1988, **124**

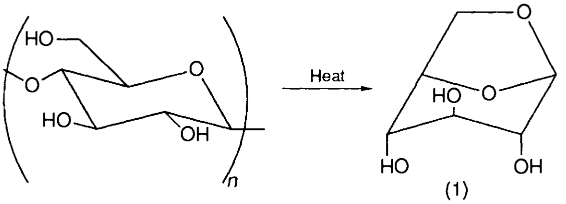
[85] G G Allan, B B Krieger, and D W Work, *J Appl Polym*, 1980, **25**, 1839

[86] A J J Straathof, H van Bekkum, and A P G Kieboom, *Recl Trav Chim Pays-Bas*, 1988, **107**, 647

Table 17 *Yield of* (1) *from glucans*[86]

Substrate	n^a	*Water content*^{b} (% w/w)	*Density* (gcm^{-3})	*Yield of* (1)^c (mg)	*Yield of* (1)^c (% w/w)
cellulose	2800	6.6	0.41	220	0.94
starch	14 000	4.2	0.95	3398	1.7
dry starch	14 000	0.0	0.95	382	1.5
amylopectin	2 000 000	11.0	0.33	226	1.0
amylose	3000	13.1	0.73	262	1.2
maltodextrin 2	50	9.5	0.46	189	0.84
maltodextrin 10	10	7.5	0.47	150	0.65
β-cyclodextrin	7	10.5	0.83	280	1.3

^{a} Chain average degree of polymerization. ^{b} Water content at the start of the reaction. ^{c} According to HPLC work-up.



Scheme 3

An irradiation time of 5 to 15 minutes was required to accomplish complete reaction for 10 to 80g of starch respectively. The yield of (1) from different glucans (Scheme 3) varied from 0.65 to 1.7% (Table 17). No correlation could be found between the reaction efficiency and chemical structure, degree of polymerization or water content, though glucan density may be an important factor. For obtaining a small amount of (1) (*ca.* 1 g) the ease of this method outweighs its low yield.

Some evidence for a specific microwave effect has been found in the cracking of neo-pentane on zeolites. The stoichiometric gas phase reaction is:

$$\text{neo-}C_5H_{12} \longrightarrow CH_4 + \text{iso-}C_4H_8$$

Using microwaves more methane is produced when zeolites are irradiated than when the zeolites are heated in a classical furnace and consequently less *iso*-butene is obtained.[87]

The reactions of methyl-2-pentane on a Pt/Al_2O_3 catalyst bed show some degree of selectivity too.[88] The range of products produced by either cracking or isomerization is shown to Table 18.

The results in Table 19 show that while most of the microwave product

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[87] G. Roussy, J. M. Thiebaut, M. Anzarmou, C. Richard, and R. Martin, *J. Microwave Power Electromag. Energy, Symp. Summ.*, 1987, 169.

[88] J. M. Thiebaut, G. Roussy, G. Maire, and F. Garin, 'International Conference on High Frequency Microwave Processing and Heating', Arnhem, Netherlands, 1989.

Table 18 *Products produced by either cracking or isomerization of methyl-2-pentane on a* Pt/Al_2O_3 *catalyst bed*

methyl-2-pentane	C1 + C5 C2 + C4 2 C3 6 C1 3 C2	cracking (C_x where x denotes the number of C atoms in the cracked hydrocarbon)
	neo-hexane (HEX) methyl-3-pentane (M3P) methylcyclopentane (MCP) benzene (BEN) cyclohexane	isomerization

Table 19 *Experimental results of reaction of methyl-2-pentane on* Pt/Al_2O_3[88]

	$S\%$	$3C_2$	C_1+C_5	C_2+C_4	$2C_3$	M3P	HEX	MCP	BEN
Microwave/ 300 °C	69 4	0 7	17 2	7 8	5 0	26 5	27 9	7 9	6 9
Classical/ 300 °C	67 1	0 6	17 5	9 4	5 7	21 0	28 4	17 4	0 3
Classical/ 325 °C	62 9	0 9	19 8	10 1	6 9	22 8	31 0	5 9	3 1

$S\%$ = Selectivity isomer/cracking

distribution can be produced conventionally, the production of benzene is substantially increased

Industrially one of the most useful chemical processes is the reduction of oxide ores to yield lower oxides and metals The strong coupling of carbon to microwave radiation has been successfully used to perform several reductions on a laboratory scale For example, TiO_2 has been reduced to TiO and V_2O_5 to V_2O_3 after 30 minutes exposure to 500 W of microwave power[89]

The reduction of iron ores through the two reactions

$$2Fe_2O_3 + 3C \longrightarrow 4Fe + 3CO_2$$

$$Fe_3O_4 + 2C \longrightarrow 3Fe + 2CO_2$$

is of particular importance in the extraction of iron from haematitic and magnetic ores In processing a range of ores with different sources of carbon in a domestic microwave oven, it has been found that the final composition depends strongly on the type of ore used[90] Final products ranging from simple white cast iron to complex super hard alloy irons have been produced The versatility of the microwave technique in the iron making process has been well demonstrated since most of the products produced conventionally have been observed as well as a few new ones

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[89] D R Baghurst and D M P Mingos unpublished results

Table 20 *Conversion (%) of pinacol to pinacolone*[91]

M^{n+}	*Conventional heating* (100 °C, 15h)	*Microwave activation* (450 W, 15 min)
Na^+	5	38
Ca^{2+}	2	23
Cu^{2+}	30	94
La^{3+}	80	94
Cr^{3+}	99	98
Al^{3+}	98	99

Table 21 *Conversion (%) of* BrC_8H_{17} *into* $CH_3CO_2C_8H_{17}$[91]

Substrate	*Conventional heating* (100 °C, 5 h)	*Microwave activation* (600 W, 10 min)
Al_2O_3	93(1)	91(3)
SiO_2	69.5(0.5)	82(12)

D. Reactions on Supports.—A novel means of accelerating a slow organic reaction is to perform the reaction on a solid support which couples effectively with microwaves. For example, the following molecular rearrangement of pinacol to pinacolone on a phyllosilicate (M^{n+}-montmorillonite) solid support has been reported:

$$\underset{\text{pinacol}}{(CH_3)_2C(OH){-}C(OH)(CH_3)_2} \xrightarrow{M^{n+}\text{-montmorillonite}} \underset{\text{pinacolone}}{CH_3{-}CO{-}C(CH_3)_3} + H_2O$$

This reaction has been studied in a conventional 650 W microwave oven using open glass or Teflon vessels.[90] Significant rate enhancements have been found compared with the conventional supported reactions. In Table 20 the percentage of pinacol transformed by 450 W of microwave power is compared with that achieved thermally at 100 °C. The reaction times were chosen so as to achieve the optimal yields: 15 hours for conventional heating and 15 minutes by microwave techniques.

The anionic alkylation (reaction of potassium acetate with 1-bromooctane) carried out either on silica gel or alumina:

$$CH_3CO_2K + C_8H_{17}Br \xrightarrow{\text{silica or alumina}} CH_3CO_2C_8H_{17} + KBr$$

has also been studied by these methods and once again dramatic rate enhancements have been found.[90] These are summarized in Table 21.

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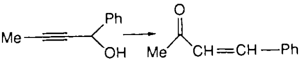
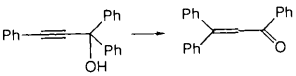
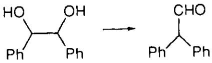
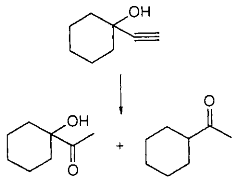
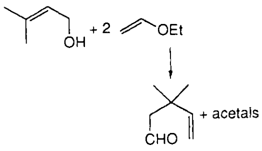
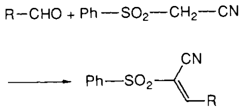
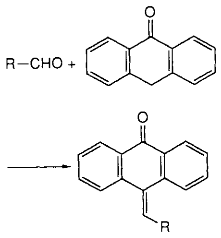
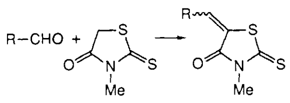
[90] B. P. Barnsley, L. Reilly, J. Jones, and J. Eshman, 'First Australian Symposium on Microwave Power Applications', Wollongong, 1989, 49.

Table 22 *Dry organic reactions by microwave heating*[92]

Reaction	*Solid support*	*Microwave heating*	*Conventional Heating*
 (2) (3)	K10 or KSF	5 min 270 W 95%	5 min < 2%
	KSF	5 min 270 W 98%	
	KSF	5 min 270 W 98%	
	KSF	5 min 270 W 51% and 41%	
	KSF	5 min 270 W 75%	5 min no aldehyde
	KF on Al_2O_3	20 min 55 W 95%	5 min 3%
	KF on Al_2O_3	20 min 55 W 90%	5 min 20%
	KF on Al_2O_3	20 min 55 W 62%	5 min 20%

Using sealed Teflon vessels similarly impressive results have been found and these are summarized in Table 22.[92] For example the acetylenic alcohol (2) when adsorbed onto K10 or KSF clay, acidic montmorillonite type phyllosilicate, at room temperature does not react. Microwave irradiation gave the rearranged product (3) in 92% yield. Typically, the alcohol in solution in CH_2Cl_2 was absorbed into 1 g of clay and irradiated with 270 W of 2.45 GHz microwave radiation for 5 minutes. A comparable thermal reaction at 170 °C gave just 2% of the rearranged product.

Summary

This review has presented the principles underlying the dielectric heating effects observed for chemical compounds in solution and in the solid state. The applications of the technique to a wide range of chemical syntheses have also been indicated. The field is in its infancy and therefore much of the effort to date has been directed towards understanding the rate enhancements of known reactions. The next few years should see the isolation of new compounds using microwave heating techniques.

Acknowledgements. The S.E.R.C. are thanked for financial support to D.R.B.

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[91] E. Gutierrez, A. Loupy, G. Bram, and E. Ruiz-Hitzky, *Tetrahedron Lett.*, 1989, **30**, 945.

[92] A. Alloum, B. Labaid, and D. Villemin, *J. Chem. Soc., Chem. Commun.*, 1989, 386.