Richard Douthwaite

Microwaves

and their application to chemical synthesis

Have you ever heated a cup of coffee or water for a minute or so in a microwave oven and then added some sugar? The liquid can boil rapidly, spitting and frothing, potentially causing nasty burns. (I don't recommend that you try it, but if you do, make sure that the cup is less than half full, use an oven glove when adding the sugar — and be very careful!) As a young boy I thought that heating conkers in a microwave for a few minutes might make them harder than the traditional method of soaking in vinegar and baking in the oven. The conkers heated all right, but they quickly began to burn, generating a truly horrendous smell. I had not appreciated the significant amount of energy emitted by a microwave oven and the potentially tremendous heating rates. Generally it is not advisable to 'put something in a microwave to see what happens', particularly if it involves closed vessels, small metal objects or especially pets!

We associate microwave ovens with rapid heating and since the 1970s they have become an integral part of our lives. Slowly the use of microwaves to drive chemical reactions is also becoming more common and in the not-too-distant future it is likely that every chemical laboratory will contain a microwave reactor. In general, reactions can be performed much more quickly using microwaves than traditional methods (such as those described in Chemistry Review, Vol. 13, No. 3, pp. 10–11) and in favourable cases the products are less contaminated with unwanted by-products.

Discovery of microwave heating

Microwaves are all around us and are used in many technologies, including microwave ovens, radar and mobile phones. Microwaves for heating are generated using a complicated device called a magnetron, which was invented in the 1920s and developed during the Second World War for the then top-secret technology, radar. After the war, further investigation of magnetrons continued in civilian industry and led one day in 1946 to the scientist Percy Spencer noticing that a chocolate bar in his pocket had melted unexpectedly. The next day he placed an egg in front of a magnetron and it exploded! (Do not try this at home. It makes a terrible mess.)

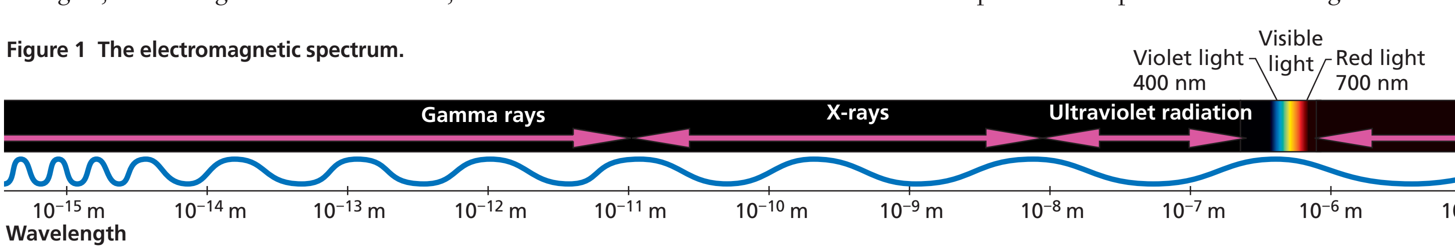
Sales of the first generation of domestic microwave oven (DMO) were slow. This was mainly because they were as big as a large fridge–freezer, weighed about the same as an adolescent rhinoceros and because rumours persisted that microwaves cause one or more of a combination of ailments including radiation poisoning, blindness and infertility. However, the decrease in weight and size, and the debunking of scare stories, has led to vast sales since the 1970s.

How do microwaves cause heating?

First of all, a bit of physics. As you may know, the electromagnetic spectrum (see Figure 1) ranges from very short gamma and cosmic waves to long wavelength radiowaves. Between these extremities is a continuum of wavelengths including ultraviolet, visible, infrared and microwaves.

As the name suggests, electromagnetic waves contain both an electric and a magnetic field component. We do not need to worry about the details here, but what is important for the application of microwaves to cooking and chemical reactions is that the electric component is responsible for heating.

Figure 1 The electromagnetic spectrum.



Box 1 Dipole moment

What is a dipole moment? Consider the structures of benzene and water shown in Figure 2. In a chemical bond the electrons are attracted to the atom with the greatest electronegativity. Oxygen has a greater electronegativity than hydrogen; carbon also has a slightly greater electronegativity than hydrogen. The slight differences in charge between adjacent atoms ($C(\delta^-)$, $H(\delta^+)$ in benzene and $O(\delta^-)$, $H(\delta^+)$ in water) is called polarisation and results in a dipole. The overall dipole (or more accurately dipole moment) of a molecule is the vector sum of the individual dipoles. What this means is that there is no dipole moment for benzene because for every dipole pointing in one direction there is an identical-sized dipole pointing in the opposite direction cancelling it out. However, for water the individual dipoles do not cancel out and therefore an overall dipole moment results. We describe molecules that have a dipole moment as **polar**. Benzene is non-polar and does not heat in a microwave. Water is polar and heats very well.

glossary

Electronegativity — the relative power of an atom in a molecule to attract an electron. (In a chemical bond, the more electronegative atom will have a partial negative charge.)

Kinetics — describes the rate of a chemical reaction.

Magnetron — a device that can generate microwaves.

Microwave — a portion of the electromagnetic spectrum of wavelength between 1 cm and 1 m.

Polarisation — distortion of electron distribution in a molecule due to differences in electronegativities.

Superheating — heating a liquid to a temperature above its boiling point at a particular pressure.

Thermodynamics — describes whether a reaction can possibly occur.

Gusto/SPL

One limitation of microwave heating is that not everything placed in a microwave oven will heat. For molecules to heat they must possess a dipole moment (i.e. be polar molecules — see Box 1 and Figure 2). What happens if we put a polar molecule in an electric field? A force is exerted on the molecule, which aligns the dipole parallel to the electric field. This is exactly analogous to a compass needle (which possesses a magnetic moment) aligning itself to a magnetic field. Now, imagine that the electric field changes direction. The dipole moment of the molecule responds to this change, trying to align parallel to the field. It takes time for the molecule to respond, in the same way that it would take time for a compass needle to respond if you waved a magnet in front of it. If the field changes quickly, the molecule will not have time to respond and nothing happens. If the field moves slowly, the molecule will be able to keep pace with the changing field. The energy required to move the molecule comes from the electric field causing the molecule to heat up slightly. If the field changes at a faster rate, more energy is transferred from the electric field to the molecule, causing significant heating. You can probably see that there must be an optimum rate of change (frequency) of an electric field to get the maximum heating. It so happens that the optimum frequency suited to heating polar molecules is in the microwave region and the electric component of microwaves therefore causes heating.

In many foods it is the water that heats when exposed to microwaves, causing the food to cook. Many fats and sugars also have a dipole moment and heat very well in a microwave. In fact, many heat much better than water, and fats and sugars have a greater heat capacity than water. This is why if you bite into a mince pie heated in a microwave, the pastry is at a nice warm temperature, yet the filling (which contains lots of sugar) can feel like your mouth is filled with volcanic magma. This type of observation has led to the myth that microwaves cook from the inside outwards, which is untrue.

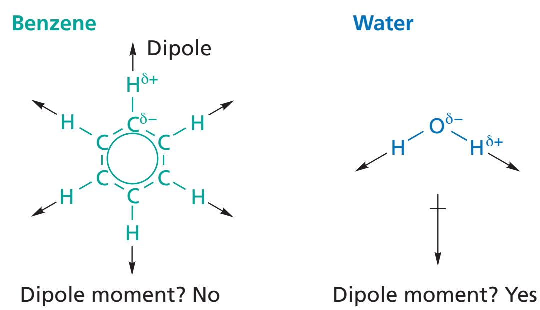
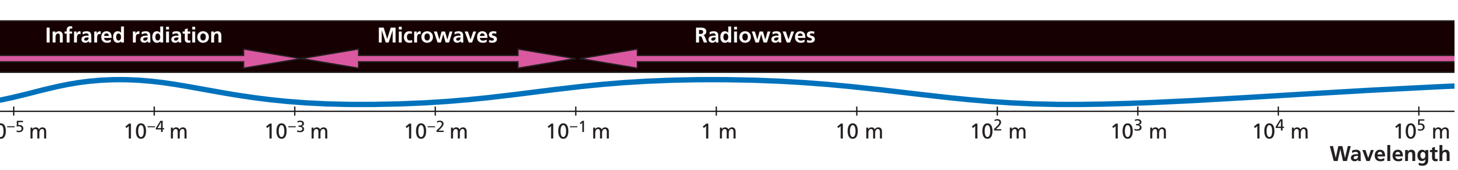


Figure 2 The structures of benzene and water.

Microwaves in chemistry

Many chemical reactions are performed in water and other polar solvents such as alcohols, and all can be accelerated by microwave heating. In the early days, chemists would buy a DMO from the high street and place the reactants in a beaker in the microwave. This works well as long as the chemicals are not too volatile or flammable. Nowadays, fancier (and unfortunately much more expensive) microwave reactors specifically for chemical laboratories are available. One of the main advantages of these new reactors is that the temperature of the reaction can be monitored and the power of the microwaves can be altered. In a DMO, a thermometer would probably explode (see Box 2) or at best not record the correct temperature because the mercury or alcohol would heat up.



Box 2 Metals in microwaves

Metal objects (including liquid metal like mercury in a thermometer) should not be used in microwave ovens. Why? Metals are characterised by electrons that are free to move throughout the entire object (which is why metals conduct electricity). The electrons collectively respond to the oscillating electric field and, depending on the size and shape of the metal object, the microwaves are either reflected or absorbed. Microwave radiation can cause rapid heating, in some metals to over 1000°C in less than a minute. However, the main problem with most metal objects is that they contain edges, for example utensils, the rim of a pan and even the decorative gold trim on expensive crockery. Conduction electrons respond to the electric field and collect at the edges of metal objects, leading to a large build-up of charge which is relieved by sparking to a nearby surface (a bit like a static electric shock). Sparking in microwaves is dangerous and certainly detrimental to continued use of the oven.

The lack of accurate temperature measurement in early experiments misled some scientists to postulate unusual 'microwave effects'. In liquid phase chemistry it is now accepted that there are no 'microwave effects' and that microwaves only increase the rate of a chemical reaction, that is, microwaves alter the kinetics but not the thermodynamics of a reaction. The massive increases in rates are due to the very efficient heating of polar liquids in microwaves that can lead to superheating. A superheated liquid is simply a liquid at a temperature above its boiling point. For example, water boils at 100°C at 1 atmosphere (≈100 kPa) but in a microwave it can easily superheat to 110°C. The water does not boil because there is not enough time to form bubbles. This is the explanation for the spitting water observation mentioned at the start of this article. Adding the sugar provides nucleation for bubble formation and the 110°C water boils immediately. It is difficult to exceed the boiling point of a solvent using traditional heating methods because there is sufficient time for bubble formation.

Examples of chemical reactions that can be accelerated using a microwave reactor include organic reactions, such as the synthesis of esters where in fact no solvent is needed because both the acid and the alcohol heat (see Figure 3). Many examples of inorganic complex formation are also known where reactions may take less than 10 minutes in a microwave but many hours or days using conventional heating methods. One practical application is the synthesis of molecules containing radioisotopes. Radioisotopes are often used in investigating metabolic pathways and in medical diagnosis, but many have a short lifetime and so rapid synthesis is important to prevent their decay before use. Microwave synthesis therefore has great potential for preparing radioisotope molecules and minimising the amount of non-radioactive material administered to a patient.

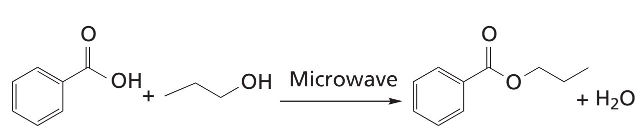


Figure 3 Ester synthesis usually takes less than 5 minutes in a microwave.

John Olive

A commercial microwave reactor that allows control of temperature. The sample is placed in the cavity (see inset).

Outlook

So is there any new science in microwaves or is it just doing reactions faster and cheaper (which nevertheless can be good for the environment)? Remember the mince pie? This is an example of what is known as differential heating, where different bits of something are heated at different rates to different temperatures. In chemistry involving polar solids, for example in catalysis, being able to heat different parts of a reaction to different temperatures on the microscopic scale is something that is not possible using traditional heating techniques.

Even if the contribution of microwave-driven reactions to fundamental chemical research is limited, the increased reaction rates and cleaner reaction conditions indicate that the socioeconomic impact promises to be significant. So next time you are in the kitchen waiting for the 'ping', remember that microwaves are more than just a means of heating your lunch quickly. ■

Richard Douthwaite *is a lecturer in the Department of Chemistry, University of York. His research interests encompass several aspects of chemical synthesis, including the use of microwave-induced plasmas for bulk synthesis of solid state materials.*

key concepts

- **Energy**
- **Electromagnetic radiation**
- **Microwaves**
- **Polar molecules**
- **Reaction kinetics**