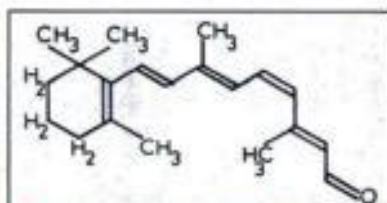


Lasers focus on fast chemistry

Some chemical reactions happen in the twinkling of an eye. New developments in the technology of lasers are helping chemists to understand ultrafast processes in biology

David Andrews



Lasers can now produce bursts of light brief enough to capture the rapid chemical changes in the retina as the eye responds to light

MANY USEFUL chemical reactions are slow and take several hours to finish. However, many other reactions that go on in gases or liquids are over in under a second. Chemists who study how rapidly chemical reactions go (called the science of reaction kinetics) consider such reactions as fast. But during the past decade, developments in the technology of pulsed lasers have allowed chemists to observe *ultrafast* chemical reactions that take less than a billionth of a second (a nanosecond). One can now buy lasers, off-the-shelf, that produce pulses only a thousandth of a nanosecond (a picosecond) long. Indeed, Chuck Shank and colleagues at Bell Telephone Laboratories in New Jersey have now produced laser pulses that last only a few femtoseconds (a millionths of a nanosecond).

It first became possible to study fast photochemical reactions in 1949. Robert Norrish and George Porter, then at Cambridge University, thought of the idea of using powerful flashes of light to break up molecules and analyse the resulting fragments. This technique, called flash photolysis, won Norrish and Porter a Nobel prize in 1960.

Flash photolysis is now a

Chuck Shank sets the record for ultra short laser pulses



well-established way of studying the photodecomposition of simple molecules. The original approach was to use a lamp filled with the inert gas xenon, placed alongside a quartz vessel containing the reacting chemicals. Banks of condensers connected to a very high voltage produced a rapid discharge in the lamp. The resulting flash lasted just one ten-thousandth of a second. Some of the light from the flash then triggered a second flash from a weaker lamp at a fixed moment, using an electronic time-delay. The second flash passed through the reacting molecules into the slit of a spectrometer. By analysing the spectra of the reactive intermediates at set times after the first flash, chemists could work out what chemical species were present and how their concentrations changed with time. This then gave a precise picture of the reaction's pathway.

Although the flash from a xenon lamp is short, it is not brief enough to study the kinetics of ultrafast reactions. Lasers can, however, produce very short pulses with a much higher intensity. They have therefore superseded flash lamps. In particular, mode-locked lasers (see the Box on the next page) produce rapid bursts of light that last less than a nanosecond.

The analytical techniques used with lasers to study

ultrafast chemistry are similar in principle to those used with flash lamps, but the more sophisticated technology allows much more precise control. A beam-splitter divides a single pulse from a laser into two parts. One part starts the chemical reaction and the other part probes the reaction after a specific time. A device called a stepping motor varies the delay between the two pulses by changing the difference in the distances the two pulses have to travel in an exact and simple way. Chemists can thus monitor the changing concentrations of the transient intermediates very accurately and can obtain comprehensive information about the kinetics of the reaction.

What kinds of molecular changes can one study with short pulses? They are usually processes that absorb energy or redistribute it within the molecule via rotation and vibration of the bonds or the whole molecule, or by exciting the electrons from a lower to a higher energy. These changes may occur within the period of a picosecond, and are often a key step in fast reactions. For example, some small molecules can complete a rotation in less than a picosecond. Molecular rotations control the fastest fluctuations in the microscopic structure of liquids. The vibrations of chemical bonds between atoms in molecules, on the other hand, may occur a hundred times in a picosecond. Vibrational "excitation" may result in the rapid transfer of energy from one part of a molecule to another. In the many simple photochemical reactions in gases, this process plays a crucial part in determining the mechanism of a reaction.

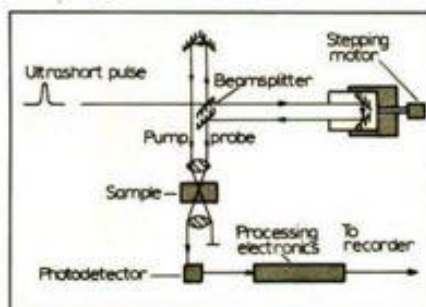
In liquids and solids, the transfer of energy can occur over a few molecules in intervals of less than a nanosecond but the efficiency of the process falls very rapidly with distance.

The development of ultrashort pulses from lasers

MEASURING the rates of ultrafast reactions requires pulses of light lasting less than a nanosecond. This means using lasers that are "mode-locked". Scientists developed the first mode-locked laser in the 1960s. A laser produces light in a narrow band of frequencies. The different frequencies which comprise the wave, or modes, are not usually in phase. This means that the modes mutually interfere, sometimes cancelling one another out. The result is a beam of regular fluctuating intensity. Under the right conditions, however, lasers can produce light with all the modes synchronised so that they constructively interfere, thus amplifying each other. This produces a train of brief intense pulses of light. The laser is then mode-locked.

It is possible to single out one pulse by using an electro-optical device called a Pockels cell, activated by an electrical spark. When combined with suitable monitoring instruments, the very short pulse duration makes it possible to observe what goes on in the instant immediately following the absorption of light—the so-called primary process.

Another key event in the development of ultrafast reaction kinetics was a discovery by R. R. Alfano and S. L. Shapiro in 1970, at Bell Telephone Laboratories. They showed that passing pulses, produced by a



mode-locked laser, through certain media generated a pulse of white light with a broad spectrum that covered the whole of the visible range. This pulse lasted only 100 femtoseconds. The effect has turned out to be surprisingly easy to produce. Even focusing a mode-locked laser into a beaker of water will do the trick. The light produced in this way is called an "ultra-fast super-continuous laser source", or supercontinuum. It is extremely useful for analysing the transient species of a reaction induced by flash photolysis. The absorption of characteristic wavelengths of light by the various products is then used to monitor their changing concentrations with a spectrometer. □

Finally, in rare cases, molecules can fluoresce in ultrafast times. Fluorescence occurs when molecules, excited by light, re-emit radiation at a different wavelength. It usually lasts for several nanoseconds. But for some dyes containing transition metals, the lifetime of the fluorescence is much shorter if the molecule can lose energy via a competing ultrafast process. The phenomenon can thus provide some useful information about these ultrafast mechanisms.

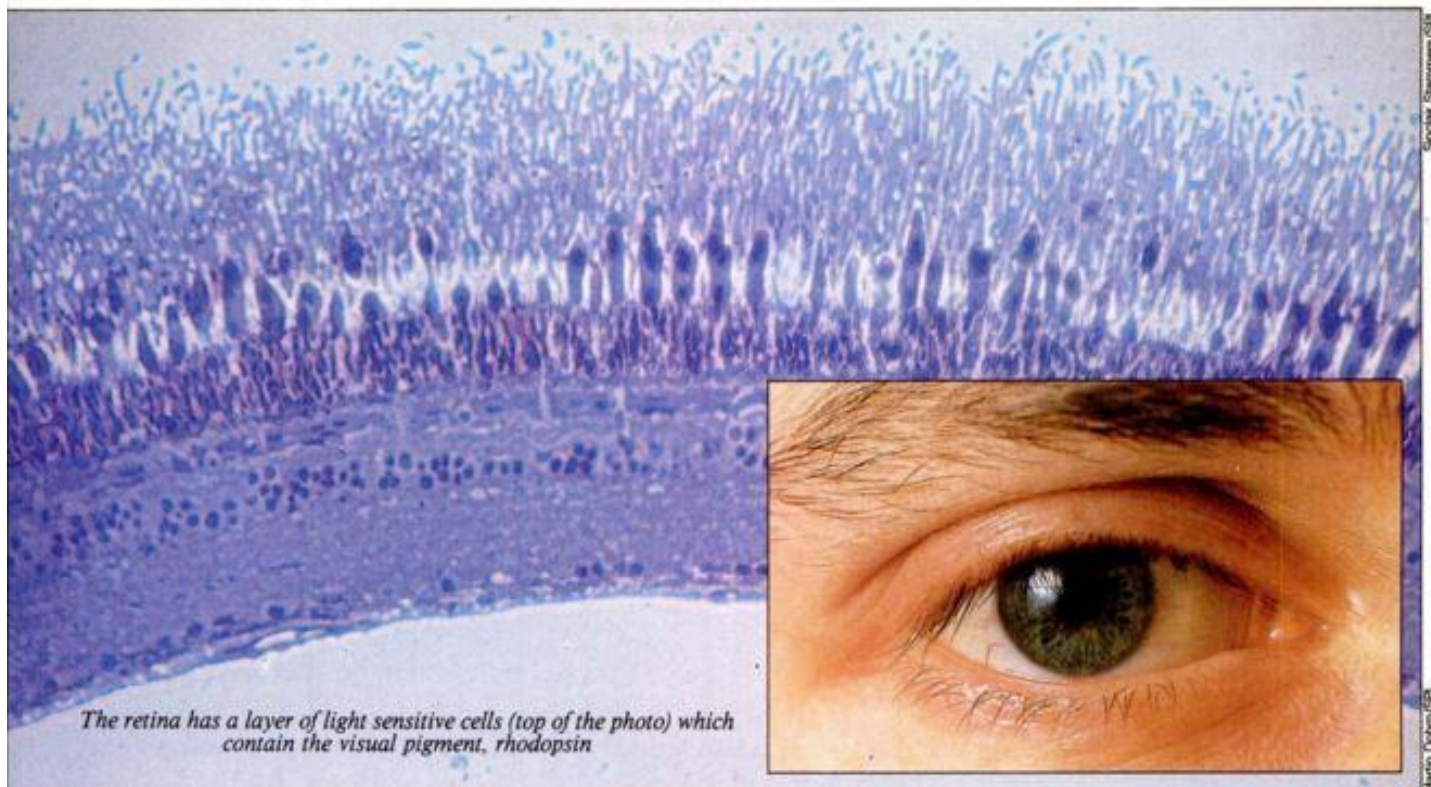
Very fast chemical reactions therefore tend to be those in which the crucial step happens within individual molecules,



Andrew Moulton/Seashol/Planet Earthpics



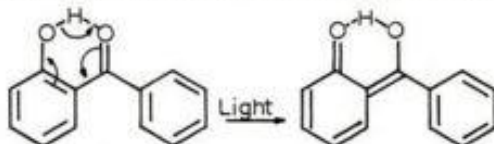
The chloroplasts found in green plants contain the so-called "antenna" pigment, chlorophyll, which absorbs light in a high speed multistep process



The retina has a layer of light sensitive cells (top of the photo) which contain the visual pigment, rhodopsin

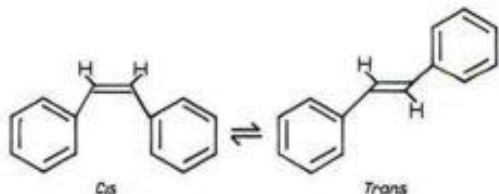
for example, the breaking of a chemical bond which follows the kind of fast processes just described. These are called unimolecular reactions. Reactions between different molecules, or bimolecular reactions, are much slower because the molecules have to move and collide before anything happens.

The change in position of a hydrogen atom within the same molecule is a typical unimolecular reaction, for example:



This swap-around takes place in about a tenth of a picosecond.

However, some kinds of rearrangements within molecules may occur without any bonds breaking. For example, the organic molecule stilbene twists round from its *cis* form, in which the benzene rings are on the same side of the central double bond, to the *trans* form, in which the rings are on

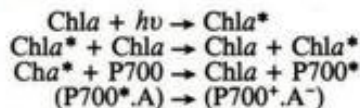


opposite sides. This happens in about 100 picoseconds.

Some of the most interesting ultrafast chemistry occurs in biology, in processes started by the absorption of light, such as photosynthesis and vision. Both processes are extremely complicated but researchers have successfully obtained important results in experiments using lasers that deliver ultrashort pulses of light.

These experiments show, for example, that photosynthesis

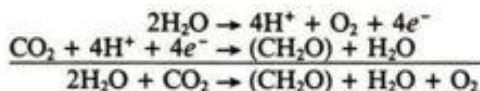
in plants has two distinct reaction sequences, known as photosystem I and photosystem II. The absorption of light initiates both processes. These systems generate the energy needed to split molecules of water in the crucial photosynthetic step. Each system depends on a different chlorophyll pigment which absorbs red light at a characteristic wavelength. In photosystem I, the chlorophyll absorbs light at a maximum wavelength of 700 nanometres; and is called P700. In photosystem II, the chlorophyll absorbs at 680 nanometres and is thus called P680. In photosystem I the primary processes are:



The asterisk means that the chlorophyll has been excited to a state of higher energy, and $h\nu$ denotes a photon. After being absorbed by the chloroplast which contains the chlorophyll, light "excites" the so-called "antenna pigment", chlorophyll, by raising the electrons to a higher energy. A rapid transfer of the energy of excitation over a series of chlorophyll molecules then follows.

Eventually, the energy ends up on a particular chlorophyll molecule, where the main reaction occurs (third equation), which results in an electron transferring to an acceptor molecule (A). Using pulsed lasers to monitor the changes in the spectra of the transient compounds formed in the intermediate steps, shows all of these primary processes to occur on the timescale of a picosecond.

The result of this sequence of reactions is the formation of a *strong* reducing agent, A^- , a species which readily donates an electron to another molecule, and a *weak* oxidant, P700^+ , which can somewhat less readily accept an electron. A similar scheme, based, on P680 chlorophyll, takes place in photosystem II. This results in formation of a *strong* oxidant P680^+ , and a *weak* reducing agent Y^- . Combining the two processes provides the driving force behind carbohydrate synthesis and the production of oxygen. The following equations summarise the chemical pathway (e^- is an electron):

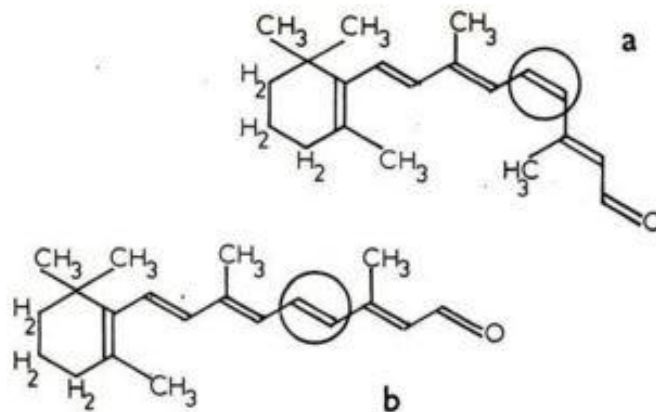


Since each of these two reactions involves four electrons, the production of a single carbohydrate unit (CH_2O) must require the absorption of eight photons. The entire photosynthetic process generally takes place in units containing about 2500 chlorophyll molecules. The closeness of these chlorophyll molecules ensures that the primary transfer of energy and electrons is fast and efficient.

Ultrafast reactions also play an important role in the mechanism of vision. Researchers are particularly interested in studying the photochemistry of rhodopsin, a visual pigment composed of more than 300 amino acids. It is the absorption of light by rhodopsin molecules in discs found in the rod cells of the retina that initiates the response of the human eye to light. There are about one billion such molecules in each cell, and more than a hundred million rod cells covering the retina.

The absorption of light takes place in a chromophore group known as retinal, a derivative of vitamin A, which absorbs most visible wavelengths of light, but centres on a wavelength of 498 nanometres in the blue-green part of the visible spectrum. Retinal (R498) is present in the form in which one double bond has a *cis* configuration, whilst all the remaining linkages are probably *trans*, as shown in (a) opposite.

Although scientists still do not know the detailed mechanism, the absorption of a photon causes the retinal to convert from a *cis* to an all-*trans* configuration shown in (b). The first evidence of a chemical change is a shift in the peak of absorption from 498 to 548 nanometres in the green region of the visible spectrum. This occurs within a picosecond of the light being absorbed. In contrast to photosynthesis, the energy of the absorbed photon does not transfer between



pigment molecules. The primary visual processes all take place within a larger molecule known as rhodopsin, of which retinal forms just a part. Subsequently, the activated rhodopsin migrates to the cell membrane, where it causes a change in the membrane's permeability to sodium ions. This initiates the response in the optic nerve.

The study of ultrafast chemistry is paradoxically a time-consuming business. It requires very expensive equipment. However the rewards in terms of results are very high indeed. As new developments in the technology produces lasers with shorter and shorter pulses, chemists can look forward to making discoveries about ultrafast reactions that could lead to useful industrial applications, such as solar energy. □

David Andrews is a lecturer in chemistry at the University of East Anglia. He is author of *Lasers in Chemistry*, Springer, Berlin, 1986.

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