affords a remarkable conservation of energy and maintenance of helical structure, with only a single base pair broken at the junction.

An important feature of Z-DNA is that, compared with B-DNA, the hydrogen-bonded base pairs are turned upside down. How this structural transition occurs is unclear, but the B–Z junction model may provide a clue. Ha *et al.* suggest that Z-DNA formation might start with the breakage of a single base pair and extrusion of the two bases. These could then swing round 180° and re-pair in the Z-DNA conformation[1]. This process would continue from the initiation point, in one or both directions, until an entire tract is transformed into a Z-DNA helix. Once formed, the ends of the Z-DNA tract and the extruded bases may zip back and forth, with dynamic fluctuations in negative superhelical density within a chromosome. This model also suggests a very low energetic barrier to Z-DNA formation, consistent with previous measurements[10].

Z-DNA may provide a sink to absorb the torsional strain left in the wake of a fleeing RNA polymerase or a transient nucleosome, or indeed any other protein complex that interacts dynamically with the DNA. It may also provide a signal for recruitment of an RNA-editing enzyme[11] or contribute to expression or repression of genes in different systems[12–15]. Although additional roles for Z-DNA are expected to emerge, the notion of a Z-DNA helix ensconced within a B-DNA chromosome and punctuated by two pairs of extruded bases presents a more reasonable, stable and energetically feasible view of this key DNA regulatory element. ■

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CATALYSIS

Gold rush

Masatake Haruta

The chemical industry would be transformed if selective oxidation of hydrocarbons could be achieved efficiently using cheap and clean oxygen from the air. Doing that with gold as a catalyst is a method gaining in allure.

The selective oxidation of hydrocarbons — the targeted addition of oxygen atoms to produce specific desired reaction products — is crucial in industrial petroleum-based chemical processes. Oxygen-containing organic compounds, such as epoxides, ketones, aldehydes, alcohols and acids, are used to produce plastics, detergents, paints, cosmetics and food additives. Oxidation catalysts are second in usage only to polymerization catalysts, accounting for 18% of total catalyst use in the United States in 1991, for example[1]. The advancement by Hutchings and colleagues of 'greener' methods for oxidation catalysis using gold (page 1132 of this issue)[2] is therefore invaluable.

Most industrial oxidation processes involve more than two reaction stages, and tend to use either chlorine or organic peroxides. In the first case, chlorinated organic intermediates are neutralized to form organic oxygenates, producing huge amounts of chloride salts and lesser, but significant, amounts of toxic chlorinated organic by-products. The alternative use of organic peroxides is expensive, and is also accompanied by the formation of by-products — economically disadvantageous if there is no market for them.

So the prospect of using molecular oxygen, O_2, as an oxidizing agent would seem seductive — it is, after all, clean and freely available from air. But the energy required to 'activate' O_2 for reaction by splitting it into its constituent atoms is 498 kilojoules per mol; this is larger than the bonding energy (431 kJ mol^{-1}) of the carbon–hydrogen bond in the most stable hydrocarbon, methane. Controlling the reactivity of atomically dissociated species of oxygen is difficult when such large amounts of energy are put into the system. The most likely course of events during the oxidation of hydrocarbons is that negatively charged oxygen radicals (O^-) are formed, which associate preferentially with electron-poor carbon atoms, leading to the displacement of hydrogen. In contrast, addition of the oxygen radicals to electron-rich carbon–carbon double bonds (epoxidation) seldom occurs.

All this means that the most common manipulation of hydrocarbons is not selective oxidation but complete oxidation (combustion), producing carbon dioxide and water and generating thermal energy. But a feasible alternative method of controlling the reactivity of oxygen species so as to obtain valuable organic oxygenates is reductive oxygen activation. This technique uses molecular hydrogen or carbon monoxide to activate oxygen under less extreme conditions, with an energy input of less than 10 kJ mol^{-1}.

Hutchings and colleagues[2] now show that nanoparticles of gold can help to activate molecular oxygen under mild conditions — at atmospheric pressure and temperatures of 60–80 °C — and so speed up oxidation reactions. Until two breakthrough discoveries in the early 1980s, gold was regarded as having almost no catalytic activity[3]. But it was then hypothesized, and experimentally confirmed, that the positive gold ion Au^{3+} can catalyse the hydrochlorination of acetylene[4]. Simultaneously, nanoparticles of gold deposited on semiconducting transition-metal oxides were shown[5] to be surprisingly active in carbon monoxide oxidation, even at −77 °C. Later, gold nanoparticles acting alone were shown to catalyse the selective oxidation of alcohol in water[6] and the epoxidation of propylene gas using titanium-based oxide supports[7].

Hutchings and colleagues' use of gold to activate molecular oxygen allows the selective oxidation not just of unsaturated hydrocarbons (generally more reactive owing to the presence of double and triple bonds), but also, in their liquid state, of the less reactive saturated hydrocarbons. In such compounds, all the bonding electrons are used up in single bonds between the constituent atoms. For example, the unsaturated hydrocarbons cyclohexene and *cis*-cyclooctene can be oxidized with 50% and 80% selectivity, respectively. Similarly, the saturated hydrocarbon cyclohexane can be converted into cyclohexanone and cyclohexanol[8] — both of which form the basis of a wide range of synthetic materials — with a combined selectivity of nearly 100%.

The authors also show that an appropriate choice of solvents allows the catalytic activity of gold to be tuned over a wide range. The product compounds change radically depending on the conditions: whether the reactant has no solvent, or whether water, nonpolar or polar organic solvents are used. All of these solvents seem to require the addition of a small amount of an initiator substance, either hydrogen peroxide or tert-butyl hydroperoxide, to kick-start the reaction. Furthermore, bismuth, which acts as a promoter for palladium and platinum catalysts in the selective oxidation of hydrocarbons, also acts as a promoter for gold. However, the mechanism of oxygen activation probably differs between the two groups of metals.

Gold's catalytic properties seem to depend less on the material on which it rests for liquid-phase oxidation[9] than they do for gas-phase oxidation[10]. However, the support material might be expected to influence at least the dispersion of the gold and thus its catalytic activity. The efficacy of gold nanoparticles as catalysts is also markedly enhanced[9,11] when the particles are less than 6 nanometres in diameter. Those used by Hutchings and colleagues[2] were relatively large, with mean diameters of around 25 nanometres, making further improvement in catalytic performance distinctly possible. Future investigations on the effects of size and support material may well reveal a far wider scope for catalysis by gold.

Exactly how gold particles activate molecular oxygen at such low temperatures remains unclear. It is equally uncertain how epoxidation works; this is the oxidation method favoured by industry but which, chemically, is the least probable route to the oxidation of hydrocarbons. Convincing answers to such questions would provide us with a valuable roadmap for pursuing green, sustainable chemistry through control of the reactivity of oxygen — which is just how enzymes act.

Gold has long been held in the imagination as a thing of never-changing beauty and value. Now it might hold our imagination as an instrument of change at the nanometre scale[12]. ■

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EVOLUTION

Along came a sea spider

Graham E. Budd and Maximilian J. Telford

An investigation of brain development in sea spiders provides hints about how the earliest arthropod head evolved. These observations are bound to provoke controversy in an already acrimonious field.

Obscure groups of animals have been making scientific waves lately[1], and few are more obscure than the sea spiders, or pycnogonids. These marine, spider-like animals differ from other arthropods, such as the true spiders, crustaceans and insects, in many ways. Their bodies are so slender that the digestive systems and gonads are squeezed into their limbs; they possess a forward-pointing proboscis with a terminal mouth; and the males brood the eggs. Flanking their unique proboscis is a pair of pincer-bearing appendages known as chelifores, which it has long been assumed are related to the pincered fangs — chelicerae — of spiders.

Work presented by Maxmen *et al.* on page 1144 of this issue[2], however, suggests that pycnogonid chelifores and spider chelicerae develop from different regions of the head and therefore cannot be equivalent. At first sight this is a rather esoteric finding. But if it is correct, it will shake up the field of arthropod evolution.

Maxmen *et al.* relied on the fact that each of an arthropod's pairs of appendages is derived from one of the repeating segments that make up the arthropod body. In addition to its appendages, each segment has a pair of nerve concentrations, or neuromeres. The authors reason that tying the appendages to a specific pair of neuromeres should reveal which segment the appendages belong to. As chelifores and chelicerae are head appendages innervated from the brain, Maxmen *et al.* considered which of the brain neuromeres each appendage is associated with during larval development. Arthropod brains are divided into three regions: protocerebral, deutocerebral and tritocerebral, from front to back. The anteriormost appendage of most living arthropods, including the spider chelicera, is innervated from the deutocerebrum[3]. What Maxmen *et al.* have now shown, in surprising contrast, is that the pycnogonid chelifores seem to be innervated from the protocerebrum — the most anterior part of the brain. The association of chelifores and chelicerae with different parts of the brain implies that the two types of limb are not equivalent, but are derived from different segments.

This result cuts across previous results based on adult structure[4], and to see the wider

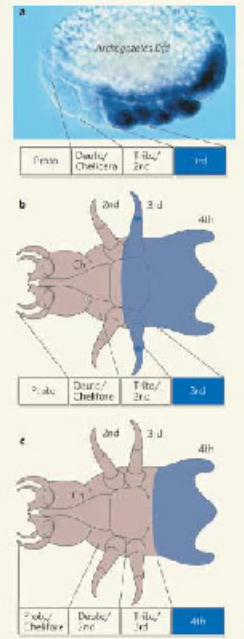

Figure 1 | Testing the results of Maxmen *et al.*[2] with Hox gene expression. a, *Deformed* (*Dfd*) expression in an arachnid embryo (the mite *Archegozetes longisetosus*[3]) compared (**b**, **c**) with that expected in a stage III pycnogonid larva under two different reconstructions. **b**, If the traditionally accepted equivalence of pycnogonid chelifores and arachnid chelicerae is correct, the anterior boundary of pycnogonid *Dfd* will be in the third appendage. **c**, If Maxmen *et al.* are correct in associating the chelifore with innervation from the protocerebrum, that boundary should be in the fourth appendage. (Appendage innervation: proto, protocerebral; deuto, deutocerebral; trito, tritocerebral. Larval image modified from ref. 10.)

implications we need some historical background. The composition of the arthropod head is one of the bitterest and longest-running problems in animal evolution. Unresolved after more than a century of debate, this sorry tale is (in)famously known as the "endless dispute"[5].

Much of the attention in this dispute has been directed towards the nervous system. It is widely agreed that the deutocerebrum, tritocerebrum and the more posterior parts of