

BIOCHEMISTRY

Breaking methane

The most powerful oxidant found in nature is compound Q, an enzymatic intermediate that oxidizes methane. New spectroscopic data have resolved the long-running controversy about Q's chemical structure. [SEE LETTER P.431](#)

AMY C. ROSENZWEIG

Bacteria that consume methane gas (CH_4) to produce methanol (CH_3OH) using dioxygen (O_2) must break two chemical bonds: the bond holding the two oxygen atoms together, and one of the extremely strong carbon–hydrogen (C–H) bonds in methane. Knowing how these bonds are broken is central to the development of biological processes for converting methane into liquid fuels. Such processes offer a possible way of dealing with the methane that is wastefully burned or leaked to the atmosphere as a result of the worldwide hydraulic fracturing (fracking) boom. On page 431 of this issue, Banerjee *et al.*¹ report the chemical structure of the molecular species that reacts with methane in the active site of one of the enzymes that converts methane to methanol, soluble methane monooxygenase (sMMO).

Abundant and cheap natural gas is composed primarily of methane, and is a crucial source of fuel and chemicals. Unfortunately, large quantities of natural gas extracted together with oil are burned at some fracking sites to the tune of gas worth US\$100 million being wasted each month². Moreover, some of this methane is vented into the atmosphere, where it acts as a potent greenhouse gas. The problem could be alleviated by converting the wasted gas into liquid fuel at fracking sites, but gas-to-liquid (GTL) conversion of methane requires large-scale, expensive 'Fischer–Tropsch' facilities that are not easily established.

An alternative that has attracted much attention is biological GTL conversion using either bacteria that oxidize methane or isolated forms of the bacteria's primary metabolic enzyme, methane monooxygenase³ (MMO). Small-scale biological GTL facilities could be deployed at remote or temporary locations, and offer advantages over Fischer–Tropsch plants because GTL conversion occurs at ambient temperature and pressure; by contrast, Fischer–Tropsch chemistry requires high temperatures and pressures. But substantial increases in the rates of MMO reactions, as well as in the fractions of the carbon and energy present in methane that are converted to product (the carbon and energy efficiencies respectively) are necessary to create a viable technology³. Understanding the details of how MMOs work is germane to making such improvements.

There are two types of MMO: a membrane-bound, copper-containing enzyme⁴ (known as pMMO) and a soluble, iron-containing enzyme (sMMO). The latter belongs to a large family of bacterial multicomponent monooxygenases that use a pair of iron ions (a dinuclear iron centre) to oxidize hydrocarbons, but it is the only member that can oxidize methane⁵. Extensive studies⁶ over the past 20 years have worked out many details of the catalytic cycle of sMMO. First, the iron ions are reduced from the +3 oxidation state to the +2 state by a reductase protein. The dinuclear iron(II) centre then reacts with dioxygen in the presence of an essential regulatory protein to form peroxodiiron(III) intermediates. Next comes the key step: the oxygen–oxygen bond is cleaved, resulting in the formation of an intermediate called compound Q, which reacts with methane to break a C–H bond. Compound Q is then converted into a complex denoted T.

Compound Q has been investigated using a range of spectroscopic and computational approaches since it was first reported more than 20 years ago⁷. In 1997, Q was assigned a 'diamond core' structure consisting of two iron ions bridged symmetrically by two single

This experiment is challenging, but the authors overcame the obstacles using a specially designed instrument.

oxygen atoms⁸. This structure was proposed on the basis of data acquired using a technique called ⁵⁷Fe-Mössbauer spectroscopy, which indicated the presence of two iron(IV) ions occupying similar electronic and geometric environments, as well as X-ray absorption spectroscopic data that showed an unusually short iron–iron (Fe–Fe) distance (2.46 ångströms). However, computational work and studies of synthetic model compounds suggested longer Fe–Fe distances⁶ (2.6 to 2.8 Å), casting doubt on the proposed structure. By the late 2000s, the tide began to turn towards another possible structure, an 'open core' containing a terminal Fe(IV)=O unit — a motif found in model compounds that can oxidize C–H bonds rapidly⁹, although not those in methane.

In principle, the true nature of Q could be determined by resonance Raman spectroscopy, which can detect molecular vibrations from the stretching of iron–oxygen bonds; the frequencies of such vibrations provide a



50 Years Ago

In a written answer in the House of Commons on February 3, the Minister of Aviation, Mr. R. Jenkins, stated that a conference, attended by all the Member States of the European Launcher Development Organization, met in Paris during January 19–21, to review the activities of the organization and to examine proposals for its future work. The cost of completing the first programmed launcher... would be higher than the original estimate, and a working group had been set up to consider the feasibility of using the technical results already achieved and the experience acquired by the organization to develop an advanced launching system making use of the most modern techniques. The system would continue to use *Blue Streak* as the first stage, and the Conference would be convened again later this year to review progress.

From *Nature* 20 February 1965

100 Years Ago

In view of the shortage of fine chemicals which are used for research purposes, we thought it advisable to issue a circular to the principal laboratories in the kingdom asking for lists of chemicals not in immediate use, so that it would be possible to put the holders of such chemicals in touch with those chemists who were in urgent need of them. The replies which have been received so far have been in most cases to the effect that the holders wish to keep their own stocks in hand, but are willing to use our bureau for the purpose of purchasing others. As this attitude is one which entirely defeats the object with which the inquiry was started, may we direct the attention of chemists to the fact that it is impossible for them all to hold and to purchase at the same time.

From *Nature* 18 February 1915