

temperature is part of a general theme of pushing the limits of thermodynamics and quantum mechanics with ultracold quantum gases. Quantum phase transitions have been explored intimately in these systems (2, 10). There is a special class of dynamical systems, called integrable, that never truly develop a temperature because their properties are different from those of a system in equilibrium with a thermal environment. Classically, integrability is opposed to chaos; chaotic dynamical systems thermalize and become thermodynamic. The borderline between integrability and chaos is described by a famous and beautiful theory, called Kolmogorov-Arnold-Moser (KAM) theory (11). To date, we do not know whether there is a KAM theory for

quantum mechanics. It is now believed that a whole new concept is needed to deal with near-integrable quantum systems, casually called prethermalization, in which physical quantities after relaxation are described by the fancy name “generalized Gibbs ensemble” (12–15).

Thermodynamics is at the heart of chemistry, engineering, and many biological questions. In ultracold quantum gases, the basic concepts of thermodynamics, positive or negative temperature, or whether a temperature concept is even relevant, are under intense and profound exploration.

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CHEMISTRY

Bioinspired Oxidation Catalysts

Martine Llargeron and Maurice-Bernard Fleury

Imines are key intermediates in the synthesis of fine chemicals and numerous biologically active compounds. They have traditionally been prepared through condensation of amines with carbonyl compounds, but the latter are extremely active and thus difficult to handle. A powerful alternative strategy involves coupling primary alcohols and amines through catalytic alcohol activation by temporary oxidation to an aldehyde (1). However, with few exceptions (2), these aerobic oxidative reactions require high reaction temperatures and catalysts that contain expensive and rare metals. Furthermore, this approach is challenging because imines can readily undergo hydrogenation (3). Recently developed metalloenzyme-like catalytic systems allow the aerobic oxidation of amines to imines under very mild conditions. They are environmentally friendly because they avoid the use of oxidants, energy-consuming processing steps, and undesirable reaction media.

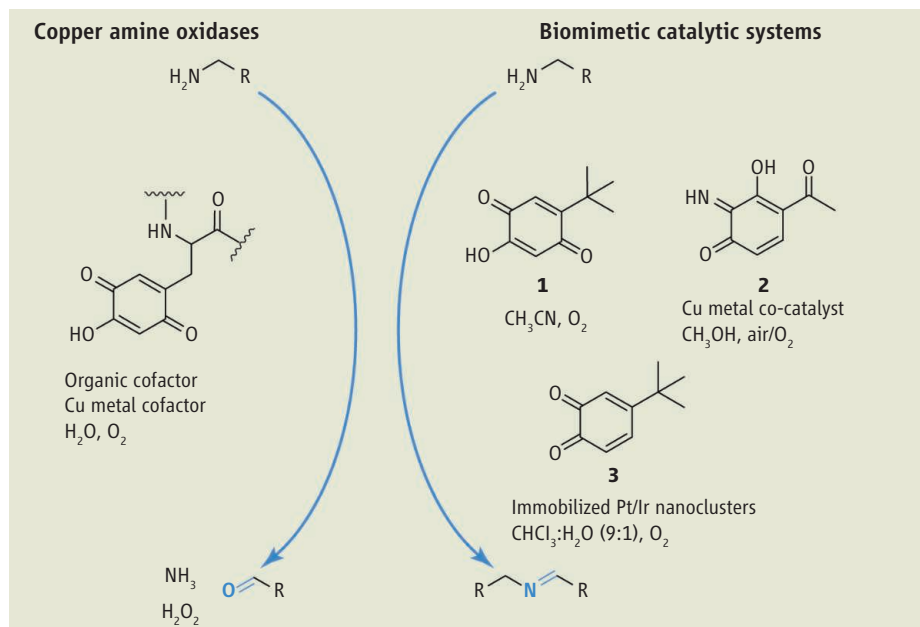
Efficient catalytic methods exist for the oxidation of secondary amines ($R^1CH_2NHR^2$) to imines ($R^1CH=NR^2$) (4), but until recently, little attention was given to the oxidation of primary amines (RCH_2NH_2), probably because the generated imines ($RCH=NH$, in which a second α -amino hydrogen is available) are generally intermediate products

that are rapidly dehydrogenated to nitriles ($RC\equiv N$) (5). Green processes have also been developed that use biocompatible transition-metal catalysts, with dioxygen or air as the sole oxidant. However, most of these methods have limitations. For example, a solvent-free copper-catalyzed synthesis of imines from primary amines uses air as a benign oxidant but requires high reaction temperatures (6). A

Metalloenzyme-like catalytic systems oxidize amines to imines under environmentally friendly conditions.

simple copper/TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) system catalyzes the aerobic oxidation of amines to imines at room temperature, but is efficient only for benzylic amines (7).

Naturally occurring metalloenzymes have long been recognized as attractive catalysts for aerobic oxidations because they can operate under mild conditions with complete che-



Biomimetic success. (Left) Copper amine oxidase enzymes catalyze the formation of aldehydes from amines. (Right) Catalyst systems developed to mimic these natural enzymes enable the aerobic oxidation of amines to imines under mild conditions.

Faculté des Sciences Pharmaceutiques et Biologiques, UMR 8638 CNRS-Université Paris Descartes, 75270 Paris Cedex 06, France. E-mail: martine.llargeron@parisdescartes.fr; maurice.fleury@parisdescartes.fr

moselectivity. Simulation of the function of these enzymes has led to the discovery of many biomimetic oxidation catalysts (8, 9).

Among metalloenzymes, copper amine oxidases (CuAOs) couple the oxidation of primary amines to aldehydes with the reduction of dioxygen to hydrogen peroxide through the synergistic action of the topaquinone (TPQ) organic cofactor and copper (see the figure, left) (10). Quinone models that mimic the active site of copper amine oxidases have yielded important insights into the mechanism by which these enzymes operate (11).

These insights have been put to use in the development of biomimetic catalytic systems for the aerobic oxidation of primary amines (see the figure, right). Building on biochemical model studies, Wendlandt and Stahl have shown that the TPQ analog 4-*tert*-butyl-2-hydroxybenzoquinone **1** is an efficient biomimetic organocatalyst for the chemoselective oxidation of primary amines to imines (12). They obtained imines in high yields (80 to 95%) from diverse benzylic amines at room temperature under 1 atm of molecular oxygen. This quinone model failed to oxidize aliphatic primary amines, but the exclusive selectivity for primary benzylic amines allowed selective formation of heterocoupled imines.

Copper amine oxidases have also inspired a biomimetic homogeneous catalytic system for the aerobic oxidation of primary amines to imines, based on the synergistic combination of copper and an *o*-iminoquinone

organocatalyst **2** first discovered from electrochemical investigations (13). Low catalyst loadings (2 mol% of **2** and 0.2 mol% of Cu) are sufficient to activate the α -C–H bond of benzylic and aliphatic amines, which were converted to alkylated imines under ambient conditions (14).

Yuan *et al.* have reported a heterogeneous catalytic system for the aerobic oxidation of amines that also shares some characteristics with copper amine oxidases (15). Their cooperative catalytic system consists of a heterogeneous Pt/Ir bimetallic nanocluster catalyst immobilized on a styrene-based copolymer support and 4-*tert*-butyl-*o*-quinone **3** as the redox-active organic cofactor. The two catalysts act together to reduce the energy of the transition state to a degree that neither catalyst can accomplish alone. With this system, the authors were able to dehydrogenate primary benzylic amines to imines in high isolated yields at room temperature under 1 atm of molecular oxygen. The catalytic system can also convert secondary amines to imines, and the heterogeneous catalyst could be recovered easily and reused up to five times without loss of activity (81 to 87% for first to fifth uses).

Many challenges remain, including the development of biomimetic catalytic systems that operate effectively at room temperature with ambient air rather than pure molecular oxygen. The development of recyclable heterogeneous nanocluster catalysts that contain

biocompatible rather than rare and precious metals would also be welcome. From a more general viewpoint, mimicking the function of amine oxidase enzymes would provide environmentally friendly organic synthesis because air is the cheaper and less polluting stoichiometric oxidant. Although challenging, this strategy would allow the chemistry of C–H bond activation to be extended to the functionalization of the α -position of primary amines under mild conditions.

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ATMOSPHERIC SCIENCE

How Was Early Earth Kept Warm?

James F. Kasting

Why do some gases cause greenhouse warming, whereas others do not? H₂O is a greenhouse gas because it has a permanent electric dipole moment (a charge separation within the molecule) that allows it to interact strongly with electromagnetic radiation. CO₂ also has an electric dipole moment, but it has to bend or stretch asymmetrically to create it, because, unlike H₂O, it is a linear molecule. N₂ and O₂ are not normally considered to be greenhouse gases, because these symmetric, diatomic molecules have no electric dipole moment and cannot bend or stretch to create one. But as Wordsworth and Pierrehumbert

show on page 64 of this issue (1), N₂ and molecular hydrogen (H₂) can be greenhouse gases under the right conditions; H₂ may have been important for Earth's Archean climate (before 2.5 billion years ago).

Researchers who study the outer planets have long known that N₂ and H₂ can contribute to the greenhouse effect. They do so through collision-induced absorption, whereby collisions between molecules allow them to absorb radiation that excites them to higher rotational states. The physics is complex (2), but the implications for the greenhouse effect are straightforward if one considers that it is the rotational states of H₂ that are being excited.

Going through the math (3) shows why H₂ can be an effective greenhouse gas on

Greenhouse warming by molecular hydrogen may have contributed to warming the surface of the early Earth.

Earth and why N₂ or O₂ cannot. For all three gases, the absorption is spread over a range of wavelengths corresponding to the populated *j* states. But an N atom is 14 times as heavy as an H atom, and the distance between the atoms is also greater in N₂ than in H₂; hence, the moment of inertia of N₂ is much larger, and its rotational energy levels are more closely spaced. As a result, the rotational constant \bar{B} is ~ 2 cm⁻¹ for N₂ and ~ 60 cm⁻¹ for H₂ (2). This means that N₂ absorbs only at wavenumbers ($1/\lambda$) < 500 cm⁻¹, where the energy radiated from Earth's surface is relatively small and where H₂O already absorbs strongly [see Fig. 1A in (1)].

What matters most for Earth's climate is the region from 830 to 1250 cm⁻¹, where H₂O and CO₂ both absorb poorly. Colli-

Geosciences Department, Pennsylvania State University, University Park, PA 16802, USA. E-mail: jfk4@psu.edu



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Martine Largeron and Maurice-Bernard Fleury
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