Preface: Forum on Small Molecules Related to Carbon-Containing Fuels

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For millennia, human transportation was fueled largely through the consumption of biomass (by humans or domestic animals) and to a lesser extent by wind. The 19th century saw a major shift to coal-fueled transportation, with trains and ships powered by steam engines. A second major shift in the fueling of transportation occurred in the 20th century, this time to petroleum. This transition was not driven by the cost or ease of obtaining energy from oil wells vs. coal mines – indeed, the cost of petroleum has always been higher than coal on a per-unit-energy basis – but rather by the tremendous technical advantages of powering engines with liquids, specifically liquid hydrocarbons.

The leading role of liquid hydrocarbons and derivatives (e.g. alcohols) as transportation fuel continues into modern times. Such liquids have a volumetric density of chemical energy greater than almost any other material, and they offer great ease of transmission - whether from an oil well to a consumer thousands of miles away, via tanker or pipeline, or from a vehicle's fuel tank into the cylinders of an internal combustion engine. While alternatives to liquids, such as hydrogen and electric power, are currently receiving great attention, it is likely that liquids will fuel much or most of our transportation for the remainder of this century and beyond.¹⁻³ In particular there are still no serious alternatives offered to the dominance of liquids in the world's fastest growing transportation sector, air travel.

Liquid fuel is currently derived mostly from petroleum – but this need not be the case. Indeed there are powerful incentives to break the traditional link between liquid fuel and petroleum. Global petroleum reserves are limited, production is likely to peak,⁴ and the striking imbalance of reserves between major consumers and producers continues to increase and to contribute to geopolitical tension. In contrast, proven natural gas reserves are growing at a remarkable pace thanks to improved methods of recovery and discovery; moreover, this growth is spread throughout the globe, including those countries that are the largest consumers of energy.³ Gas-to-liquid (GTL) conversion of methane is already conducted commercially, but on a fairly limited scale; the development of GTL methods that are more efficient, versatile, and economical represents a tremendous opportunity. Moreover, natural gas is flared globally on a scale that represents a tremendous waste of energy; better methods for conversion to liquids could allow us to instead use that energy productively.

Natural gas, and light alkanes generally, are thus a highly attractive source of both carbon and chemical energy. But like petroleum, gas is a finite resource. And perhaps of even greater concern, obtaining our energy from natural gas, as from petroleum, requires the formation of CO₂. At the very least, as we emit CO₂ at the present scale, we are taking extraordinary global-scale risks.

Thus, in the long term, the *energy* for our transportation must be derived entirely from a source other than fossil fuel, whether that source is solar, wind, fission, fusion, or some other alternative. In that case, there is only one obvious source of the *carbon* for liquid fuels: conveniently enough, it is the same molecule whose atmospheric abundance we wish to avoid increasing, CO₂.

Chemists are therefore presented with two great challenges. At first glance these seem nearly opposite: development of better ways to (partially) oxidize carbon in its lowest oxidation state (in methane and other light alkanes) and better ways to reduce carbon in its highest oxidation state (CO₂). From the perspective of scientists interested in catalysis there are some obvious relationships; catalysts, after all, necessarily work in both directions.

In this Forum issue comprising selected articles from experts in the field, the chemistry of light alkane oxygenation is explored by Thomas Strassner⁵ and Lawrence Que, Jr.⁶ Strassner offers an overview of the functionalization of light alkanes by three approaches, each exemplified by systems under study in his laboratory. These approaches are: (1) C-H activation by a transition metal catalyst, followed by oxidation by a redox mediator, with O₂ as the ultimate oxidant. The system explored in depth in this paper involves C-H activation by a Pd(II)[bis(N-heterocyclic-carbene)](trifluoroacetate) complex, which operates via concerted metallation deprotonation (CMD) in which Pd-C and acetate-O-H bonds are formed concurrently. Oxidation is then mediated by bromine and vanadates. (2) Reactions of methane with O₂ catalyzed by cobalt salts that likely operate via oxygen-based radical mechanisms. (3) Reactions with main group compounds, particularly high oxidation state compounds of iodine such as iodate salts, which could ultimately be regenerated with O₂. These have been proposed to operate via a mechanism that is, interestingly, related to the CMD pathway proposed for the Pd complexes.⁷

The Forum article by Que affords an overview of alkane C-H bond cleavage by oxoiron(IV) complexes, both heme- and non-heme-coordinated. Such species operate via hydrogen atom transfer to the oxo group. Oxoiron heme complexes comprise the active states of cytochromes P450, which are ubiquitous in Nature. They are the most well studied natural systems for the cleavage of strong C-H bonds and have inspired many synthetic models. Non-heme iron oxygenases, particularly the dinuclear soluble methane monooxygenases (sMMO), but also mononuclear species, have more recently been the subject of extensive study. In this article, Que and co-workers report new

results on the oxidation of strong C–H bonds by a synthetic oxoiron(IV) species that is generated *in situ* using O₂ at ambient conditions.

Metal oxides are also used by Copéret⁸ to cleave C-H bonds, but in a fashion that is mechanistically and stoichiometrically very different from oxoiron chemistry. Cr(III) silicates are found to cleave C-H bonds heterolytically, giving Cr-C and O-H bonds. In the case of ethylene C-H activation, formation of the Cr-vinyl species is found to lead to olefin polymerization. In the case of propane, the resulting Cr-bound propyl group can undergo β-H elimination, leading to propene. This chemistry offers important implications for the liquefaction of light alkanes.

In all of the examples above, inorganic chemists may tend to focus on the metal (or main group heavy atom) center. But it is interesting to note that in all of these examples, it is likely that the C-H bond cleavage event is driven – partly or fully – by the formation of an O-H bond.

Robert Crabtree's article⁹ covers a middle ground between the two major areas of focus in this issue: reduction of CO₂ and oxidation of methane (or other alkanes). Crabtree and co-workers report iridium-based catalysts for the dehydrogenation (oxidation) of methanol, a reaction of obvious interest in the context of methanol as a hydrogen carrier, and of great interest in the context of chemical synthesis. The Ir complexes catalyze dehydrogenation in basic KOH solution to give primarily potassium formate and two moles of H₂. To a limited extent the reaction proceeds further, to give CO₂ and an additional mole of H₂; this is the reverse of a CO₂ hydrogenation reaction. The same catalysts are also found to transfer hydrogen to ketones and imines, thus allowing chemists to exploit methanol as a cheap and convenient source of hydrogen for chemical transformations. Additionally, so-called H-borrowing reactions are catalyzed. These involve dehydrogenation of methanol to give formaldehyde which then undergoes electrophilic attack by amines; upon "return" of the "borrowed" hydrogen, the net reaction is methylation of the amine.

Because CO₂ is so thermodynamically stable it is very difficult to activate and convert to useful chemicals or fuels. One-electron reduction of CO₂ takes place at -1.9 V vs. NHE, indicating a highly energetically demanding reaction. However, proton-coupled multi-electron transfer reactions of CO₂ to form CO, HCOOH, and MeOH occur at much more favorable potentials using transition metal catalysts.

Koji Tanaka¹⁰ and his coworker present a summary their work on reductive activation of CO₂ at the metal center or sulfur ligands of transition metal complexes using electrons as the energy source. Ruthenium carbonyl complexes bearing additional ligands, for example [Ru(bpy)₂(CO)₂]²⁺ (bpy = 2,2'-bipyridine), were discovered by Tanaka in 1987 and are among the most well-known CO₂ reduction catalysts currently being used to produce CO and formate. They investigated not only acid-base reactions of [Ru(bpy)₂(CO)₂]²⁺ to form [Ru(bpy)₂(CO)(COOH)]⁺ and

[Ru(bpy)₂(CO)(CO₂)], but also reactions with NaBH₄ to produce [Ru(bpy)₂(CO)(CHO)]⁺, [Ru(bpy)₂(CO)(CH₂OH)]⁺ and [Ru(bpy)₂(CO)(CH₃)]⁺ (precursors of formaldehyde, methanol and methane, respectively). [Ru(bpy)₂(CO)₂]²⁺ can also catalyze the photochemical reaction of alkylamines to form dialkylformamides with Ru(bpy)₃²⁺ as a photosensitizer. Since CO₂ is introduced to an organic moiety in a biological system, Tanaka's investigations related to the biological systems are also described here.

Ishitani's¹¹ group focuses on photochemical CO₂ reduction using Re(α -diimine)(CO)_n-type mono-nuclear and multi-nuclear complexes (n = 2,3) and supramolecular Ru-Ru, Ru-Re, and Os-Re systems using sacrificial electron donors such as 1-benzyl-1,4-dihydronicotinamide (BNAH) and 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (BIH) in dimethylformamide/triethanolamine solutions to yield CO from CO₂. They review three types of efficient photocatalytic systems, and compare them to previously studied systems by other groups. The first two systems require sacrificial electron donors. It should be noted that their hybrid photocatalyst (Ru-Ru) anchored on TaON decorated with Ag nanoparticles is an artificial Z-scheme system and gives HCOOH from CO₂ and HCHO from the solvent MeOH upon irradiation. Although electrons and protons from methanol seem to be used to reduce CO₂, this represents a promising direction in which an endergonic reaction is activated by visible light.

Sato's¹² group has been investigating photocatalytic CO₂ reduction coupled with water oxidation using innovative semiconductor/metal complex hydride systems in water. They review advantages and disadvantages of previous photocatalytic systems including a system with a metal complex as a water oxidation catalyst with a sacrificial electron acceptor (i.e., oxidative half reaction), a system with a CO₂-reduction molecular catalyst with a sacrificial electron donor in an organic solvent (i.e., reductive half reaction), and a system coupling these two reactions to remove sacrificial reagents. In their new systems, CO₂ photoreduction at the immobilized molecular catalysts and water photooxidation at the semiconductors simultaneously occur under sunlight irradiation with conversion efficiency from solar to chemical energy ca. 0.08 %. The source of electrons and protons were confirmed by labeling experiments. This represents remarkable progress considering that the efficiency of natural photosynthesis is ≤ 1 %.

Himeda¹³ and co-workers propose CO₂ hydrogenation as an alternative to CO₂ reduction by artificial photosynthesis, which faces complicated challenges (low efficiency, low durability, low selectivity of products, coupling of reductive and oxidative reactions under experimental conditions, etc.). While hydrogen is considered a next-generation clean energy fuel, it is difficult to handle and transport. Formic acid, formed by the hydrogenation of CO₂, contains only 4.4% hydrogen by weight, considerably lower than that of methanol. It does, however, offer several advantages compared with methanol. Formic acid is less toxic and it is non-flammable. With present technology,

the release of H₂ at ambient temperature from formic acid is possible, unlike from methanol. Moreover, direct formic acid fuel cells are currently much more efficient than direct methanol fuel cells.¹⁴ Himeda's group carries out efficient interconversion of CO₂ and formic acid under mild conditions using a Cp*Ir complex with bio-inspired proton-responsive ligands in water by simply changing the pH.

Peters and Fong¹⁵ investigate CO₂ reduction using earth-abundant Fe complexes with tris-phosphinate ligands containing Si, C, N, or B as a coordinating element. The stability and the reaction rate are much lower in a THF solution containing MeOH than those of Himeda's Ir complexes, but the isolation and spectroscopic characterization of reaction intermediates may facilitate future development of these systems. Using the experimentally determined hydricity ($\Delta G_{H^+} = 54.3 \pm 0.9$ kcal/mol) of one of the Fe–H species (which is thermodynamically too weak to transfer H[−] to free CO₂ to produce HCO₂[−]) and the pK_a of the conjugate acid (15.9 ± 0.7) in acetonitrile, Peters and Fong present an analysis of the mechanism and influence of solvent that suggest new routes to the development of improved catalysts.

As this Forum Preface goes to press, we have recently experienced the warmest year in recorded history (2014) across the globe,¹⁶ while many parts of the world are experiencing terrible turmoil and violence that is clearly connected to the politics and economics of petroleum production. It is ultimately inevitable that we end humanity's dependence on petroleum as the primary source of our liquid fuels, and it is critical that we do it sooner rather than later. The catalytic transformations of small carbon-containing molecules thus represent an area of research that offers some of the greatest challenges and opportunities in chemistry today. The articles in this Forum present a sampling of some of the most exciting ongoing work in this area from around the world. We hope this Forum serves to stimulate and inform future efforts in this field, and we express our thanks to the contributing authors.

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References

- (1) Brandt, A. R.; Millard-Ball, A.; Ganser, M.; Gorelick, S. M. *Environ. Sci. Technol.* **2013**, *47*, 8031-8041.
- (2) *International Energy Outlook 2014*, U.S. Energy Information Administration [http://www.eia.gov/forecasts/ieo/pdf/0484\(2014\).pdf](http://www.eia.gov/forecasts/ieo/pdf/0484(2014).pdf)

- (3) *BP Energy Outlook 2035, February 2015*
http://www.bp.com/content/dam/bp/pdf/Energy-economics/energy-outlook-2015/Energy_Outlook_2035_booklet.pdf
- (4) Miller, R. G.; Sorrell, S. R. *Philos. Trans. Roy. Soc. London Ser. A* **2013**, 372.
- (5) Munz, D.; Strassner, T. *Inorg. Chem.* **2015**, 54, page number.
- (6) Kleespies, S. T.; Oloo, W. N.; Mukherjee, A.; Que, L., Jr. *Inorg. Chem.* **2015**, 54, page number.
- (7) Konnick, M. M.; Hashiguchi, B. G.; Devarajan, D.; Boaz, N. C.; Gunnoe, T. B.; Groves, J. T.; Gunsalus, N.; Ess, D. H.; Periana, R. A. *Angew. Chem., Intl. Ed.* **2014**, 53, 10490-10494.
- (8) Conley, M. P.; Delley, M. F.; Núñez-Zarur, F.; Comas-Vives, A.; Copéret, C. *Inorg. Chem.* **2015**, 54, page number.
- (9) Campos, J.; Sharninghausen, L. S.; Manas, M. G.; Crabtree, R. H. *Inorg. Chem.* **2015**, 54, page number.
- (10) Kobayashi, K.; Tanaka, K. *Inorg. Chem.* **2015**, 54, page number.
- (11) Sahara, G.; Ishitani, O. *Inorg. Chem.* **2015**, 54, page number.
- (12) Sato, S.; Arai, T.; Morikawa, T. *Inorg. Chem.* **2015**, 54, page number.
- (13) Onishi, N.; Xu, S.; Manaka, Y.; Suna, Y.; Wang, W.-H.; Muckerman, J. T.; Fujita, E.; Himeda, Y. *Inorg. Chem.* **2015**, 54, page number.
- (14) (a) Jiang, H. L.; Singh, S. K.; Yan, J. M.; Zhang, X. B.; Xu, Q. *ChemSusChem* **2010**, 3, 541-549. (b) Loges, B.; Boddien, A.; Gartner, F.; Junge, H.; Beller, M., *Top. Catal.* **2010**, 53, 902-914.
- (15) Fong, H.; Peters, J. C. *Inorg. Chem.* **2015**, 54, page number.
- (16) *NASA, NOAA Find 2014 Warmest Year in Modern Record, National Aeronautics and Space Administration, Release 15-010, January 16, 2015*
<http://www.nasa.gov/press/2015/january/nasa-determines-2014-warmest-year-in-modern-record>