ANNOUNCEMENT

UNITED STATES DEPARTMENT OF ENERGY (DOE)
Scientific and Technical Information (STI) For Financial Assistance Recipients and Non-M&O/M&I Contractors

OMB Control No.
1910-1400

PART I: STI PRODUCT DESCRIPTION

(To be completed by Recipient/Contractor

A. STI Product Identifiers

1. REPORT/PRODUCT NUMBER(s)

NONE

2. DOE AWARD/CONTRACT NUMBER(s)

DE-FG02-06ER15799

3. OTHER IDENTIFYING NUMBER(s)

DOE180

H. Sponsoring DOE Program Office

Office of Science, U.S. Department of Energy

I. Subject Categories *(list primary one first)*

37 – Inorganic, Organic, Physical and Analytical Chemistry

Keywords Oxidation Catalysis, Hydrocarbon functionalization, Environmentally friendly reagents, earth abundant metals, bioinspired catalysis, oxygen activation, reaction mechanisms, kinetics

B. Recipient/Contractor

J. Description/Abstract

In modern era of scarce resources, developing chemical processes that can eventually generate useful materials and fuels from readily available, simple, cheap, renewable starting materials is of paramount importance. Small molecules, such as dioxygen, dinitrogen, water, or carbon dioxide, can be viewed as ideal sources of oxygen, nitrogen, or carbon atoms in synthetic applications. Living organisms perfected the art of utilizing small molecules in biosynthesis and in generating energy; photosynthesis, which couples carbohydrate synthesis from carbon dioxide with photocatalytic water splitting, is but one impressive example of possible catalytic processes. Small molecule activation in synthetic systems remains challenging, and current efforts are focused on developing catalytic reactions that can convert small molecules into useful building blocks for generating more complicated organic molecules, including fuels. Modeling nature is attractive in many respects, including the possibility to use non-toxic, earth-abundant metals in catalysis. Specific systems investigated in our work include biomimetic catalytic oxidations with dioxygen, hydrogen peroxide, and related oxygen atom donors. More recently, a new direction was been also pursued in the group, fixation of carbon dioxide with transition metal complexes.

Mechanistic understanding of biomimetic metal-catalyzed oxidations is critical for the design of functional models of metalloenzymes, and ultimately for the rational synthesis of useful, selective and efficient oxidation catalysts utilizing dioxygen and hydrogen peroxide as terminal oxidants. All iron oxidases and oxygenases (both mononuclear and dinuclear) utilize metal-centered intermediates as reactive species in selective substrate oxidation. In contrast, free radical pathways (Fenton chemistry) are common for traditional inorganic iron compounds, producing hydroxyl radicals as very active, non-selective oxidants. Recent developments, however, changed this situation. Growing families of synthetic iron complexes that resemble active sites of metalloenzymes produce metal-based intermediates (rather than hydroxyl radicals) in reactions with oxygen donors. These complexes are very promising for selective oxygen and peroxide activation. In order to understand the mechanisms of metal-based small molecule activation, kinetically competent metal-oxygen intermediates must be identified.

One of the grand challenges identified by the Department of Energy workshop "Catalysis for Energy" is **understanding mechanisms and dynamics of catalyzed reactions**. The research summarized herein focuses on detailed characterization of the formation and reactivity of various iron-peroxo- and iron-oxo intermediates that are involved in catalysis. Rates of rapid reactions were studied at low temperatures by a specialized technique termed cryogenic stopped-flow spectrophotometry. These measurements identified reaction conditions which favor the formation of catalytically competent oxidants. Chemical structures of reactive complexes was determined, and new, efficient catalysts for hydrocarbon oxidation were synthesized. Importantly, these catalysts are selective, they promote oxidation of hydrocarbons at a specific site. The catalysts are also efficient and robust, hundreds of cycles of substrate oxidation occur within minutes at room temperature. Furthermore, they enable utilization of environmentally friendly oxidants, such as hydrogen peroxide, which produces water as the only byproduct. Mechanistic insights uncovered the role of various acid-containing additives in catalytic oxidations. Proton delivery to the active catalytic sites facilitated oxidations, similarly to the catalytic pathways in metal-containing enzymes. Under certain conditions, two metals in one complex can act in concert, modeling the reactivity of a

Tufts University

C. STI Product Title

Mechanisms-Based Design of Green Oxidation Catalysts

D. Author(s)

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E. STI Product Issue Date/Date of Publication

03/12/2015 (mm/dd/yyyy)

F. STI Product Type *(Select only one)*

X 1. TECHNICAL REPORT

X *Final* ☐ *Other (specify)*

☐ 2. CONFERENCE PAPER/PROCEEDINGS

Conference Information (title, location, dates)

☐ 3. JOURNAL ARTICLE

a. TYPE: ☐ *Announcement Citation Only* ☐ *Preprint* ☐ *Postprint*

b. JOURNAL NAME

c. VOLUME *d. ISSUE*

e. SERIAL IDENTIFIER (e.g. ISSN or CODEN)

☐ OTHER, SPECIFY

G. STI Product Reporting Period (mm/dd/yyyy)

07/01/2006 *Thru* *06/30/2014*

bacterial enzyme which converts methane into methanol.

In related studies, a family of nickel complexes that react with carbon dioxide at the rates comparable to enzyme carbonic anhydrase, was discovered. Sequestration and chemical utilization of carbon dioxide is one of the important goals in energy production.

K. Intellectual Property/Distribution Limitations

(must select at least one; if uncertain contact your Contracting Officer (CO))

X 1. UNLIMITED ANNOUNCEMENT *(available to U.S. and non-U.S. public; the Government assumes no liability for disclosure of such data)*

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(Sections are marked as restricted distribution pursuant to 35 USC 205)

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If other, specify
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Release date (Required,
(No more than 4 years from date listed in part 1.E above)

☐ 6. SMALL BUSINESS TRANSFER (STTR) DATA
Release date (Required,
No more than 4 years from date listed in part 1.E above)

☐ 7. OFFICE OF NUCLEAR ENERGY APPLIED TECHNOLOGY

L. Recipient/Contractor Point of Contact *Contact for additional information (contact or organization name to be included in published citations and who would receive any external questions about the content of the STI Product or the research contained therein)*

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E-mail *Phone*

Tufts University
Organization

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PART II: STI PRODUCT MEDIA/FORMAT and LOCATION/TRANSMISSION

(To be completed by Recipient/Contractor)

A. Media/Format Information:

1. MEDIUM OF STI PRODUCT IS:
   - ☐ Electronic Document ☐ Computer medium
   - ☐ Audiovisual material ☐ Paper ☐ No full-text
2. SIZE OF STI PRODUCT _____
3. SPECIFY FILE FORMAT OF ELECTRONIC DOCUMENT BEING TRANSMITTED, INDICATE:
   - ☐ SGML ☐ HTML ☐ XML ☐ PDF Normal ☐ PDF Image
   - ☐ WP-Indicate Version *(5.0 or greater)* _____
     Platform/operating system _____
   - ☐ MS-Indicate Version *(5.0 or greater)* _____
     Platform/operating system _____
   - ☐ Postscript _____
4. IF COMPUTER MEDIUM OR AUDIOVISUAL
   - a. Quantity/type *(specify)* _____
   - b. Machine compatibility *(specify)* _____
   - c. Other information about product format a user needs to know: _____

B. Transmission Information:

STI PRODUCT IS BEING TRANSMITTED:

- ☐ 1. Electronic via Elink
- ☐ 2. Via mail or shipment to address indicated in award document *(Paper products, CD-ROM, diskettes, videocassettes, et.)*

_____

- ☐ 2a. Information product file name *(of transmitted electronic format)*

_____

PART III: STI PRODUCT REVIEW/RELEASE INFORMATION

(To be completed by DOE)

A. STI Product Reporting Requirement Review:

- ☐ 1. THIS DELIVERABLE COMPLETES ALL REQUIRED DELIVERABLES FOR THIS AWARD
- ☐ 2. THIS DELIVERABLE FULFILLS A TECHNICAL REPORTING REQUIREMENT, BUT SHOULD NOT BE DISSEMINATED BEYOND DOE.

B. DOE Releasing Official

- ☐ 1. I VERIFY THAT ALL NECESSARY REVIEWS HAVE BEEN COMPLETED AS DESCRIBED IN DOE G 241.1-1A, PART II, SECTION 3.0 AND THAT THE STI PRODUCT SHOULD BE RELEASED IN ACCORDANCE WITH THE INTELLECTUAL PROPERTY/DISTRIBUTION LIMITATION ABOVE.

Released by *(name)* _____

Date _____
(mm/dd/yyyy)

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INSTRUCTIONS

Purpose: DOE F 241.3 provides the Office of Scientific and Technical Information (OSTI) information required to appropriately identify, process, and/or announce and disseminate the results of work funded by the U.S. Department of Energy (DOE). For general information or assistance with this form, contact OSTI at (865) 241-6435, or at the following e-mail address: 241user@adonis.osti.gov.

When to use: Submit this form with each scientific and technical information (STI) Product. Electronic format is the preferred method for submitting the announcement record and STI Product. When submitting electronically, use the electronic version of the form (http://www.osti.gov/elink; discuss with your DOE Contracting Officer).

Describing the data fields: Descriptions of the various DOE F 241.3 data fields, STI Products, format, etc., can be found in ATTACHMENT 3 and other sections of the DOE G 241.1-1A, Guide to the Management of Scientific and Technical Information. Available online at http://www.osti.gov/stip/

DOE Financial Assistance Recipients/Contractors Recipients and Contractors should complete Parts I and II of the form and forward the form along with the STI product to the DOE Contracting Officer who will complete the rest of the form and submit the package to OSTI.

NOTE: Sensitive, proprietary, or other STI Products for which access is restricted by statute or regulation shall not be transmitted via open systems networks (e.g., the Internet) unless authorization and/or encryption has been coordinated with OSTI in advance. This form, unless it in itself is classified, can be transmitted via open systems networks (.e.g, the Internet).

RECORD STATUS - This is a required field. The record status identifies the announcement record or the STI Product as new, or revised. If the record status is not provided, the record is considered "New."

Part I: STI PRODUCT DESCRIPTION (To be completed by Recipient/Contractor)

A. STI PRODUCT IDENTIFIERS.

1. **Report/Product Number(s).** This is a required field. The unique primary report or product number assigned to the STI product. If a report number is not provided, the word "NONE" should be entered.

Following are examples of report number formats for multiple volumes, parts, or revisions:

DOE/ID/13734-2

DOE/NE/01834--1-Pt. 1

More than one report number may be provided. Multiple numbers are separated with a semicolon and a space. When more than one number is entered, the first number, considered the primary number, should identify the submitting organization. All other numbers are considered secondary numbers.

2. DOE Award/Contract Number(s). This is a required field. Enter the DOE award/contract number under which the work was funded. Additional DOE award/contract numbers related to the product may be entered. Multiple numbers are separated with a semicolon and a space. When more than one number is entered, the first number is considered the primary number.

3. Other Identifying Number(s). An additional unique identifying number assigned to the STI product. (e.g., CRADA numbers, Non-DOE contract numbers). More than one other identifying number may be provided. Multiple numbers are separated with a semicolon and a space.

B. RECIPIENT/CONTRACTOR - This is a required field. Provide the name and location of the organization that performed the research or issued the STI product. More than one organization may be provided; separate multiples with a semicolon and a space.

Example: University of Tennessee, Knoxville, TN

C. STI PRODUCT TITLE - This is a required field. Provide the title exactly as given on the product itself, including part, volume, edition, and similar information.

D. AUTHOR(s) - This is a required field. Provide the name of the author (last name first) of the STI product. More than one author may be provided; separate multiple entries with a semicolon and a space. If an author does not exist, the word "None" should be entered.

Examples: Jones, T.M.; Markay, Arthur R. III
Fields, J.M., ed.

Author(s) E-mail Address(es). Provide the e-mail address for each author. Multiples may be provided; they should be listed in the same order as the authors and should be separated by a semicolon and a space.

E. STI PRODUCT ISSUE DATE/DATE OF PUBLICATION - This is a required field. Provide the date when the information product was published or issued.

F. STI PRODUCT TYPE - This is a required field. It should agree with the reporting requirement identifier in the reporting requirements checklist; federal assistance reporting checklist; or in the statement of work if the product is a required deliverable that warrants accountability.

1. **Technical Report**. Identify the type of technical report provided.

2. **Conference Paper.** Provide all available conference information. An agenda alone is not sufficient for announcement.

3. **Journal Article.** Provide all available Journal Article information.

G. STI PRODUCT REPORTING PERIOD. Specify the beginning and ending dates of the period covered by the STI product.

H. SPONSORING DOE PROGRAM OFFICE - Enter the name or acronym of the DOE Program Office (e.g., Office of Science or SC) providing the funding for the work described in the STI product. For projects funded by more than one Program Office, indicate all sources of the DOE funding in descending order of dollar amount of funding appropriated. Separate multiple program offices with a semicolon and a space. If no sponsoring DOE Program Office is provided, "DOE" will be the sponsor.

I. SUBJECT CATEGORIES - Select one or more categories from the list provided. List the primary one first. A list of subject categories is available at (http://www.osti.gov/elink/).

Keywords. Provide terms which describe the content of the publication. More than one term may be entered; separate multiple terms with a semicolon and a space.

J. DESCRIPTION/ABSTRACT - Provide a clear, concise, and publicly releasable English language summary of the information content of the STI product. The abstract length should be no more than 5,000 characters. If you are utilizing paper media, you may provide via attachment.

K. INTELLECTUAL PROPERTY/DISTRIBUTION LIMITATIONS - This is a required field. STI products should be written for public release; therefore, STI products should not contain proprietary, classified or any information subject to export control. Recipients/Contractors are responsible for notifying their DOE contracting officer if the document contains other than unclassified data before submitting to the DOE address in the award document. Recommendations to restrict access to STI products must have a legal basis or be accompanied by written programmatic guidance. For questions concerning current laws and guidance, refer to Part II or ATTACHMENT 7 of the DOE G 241.1-1A, Guide to the Management of Scientific and Technical Information, or contact your DOE Contracting Officer.

1. **Unlimited Announcement**. The unrestricted, unlimited distribution of the product (will be made publicly available). The Government assumes no liability for disclosure of such data.

2. **Copyrighted Material**. A copyright restriction on part or all of the contents of the STI product may affect the reproduction and distribution of the product by OSTI. Any restriction must be specified.

3. **Patentable Material**. Provide all applicable patent information.

4-6. No special instructions.

7. Office of Nuclear Energy Applied Technology pursuant to 10 CFR 810.

L. RECIPIENT/CONTRACTOR POINT OF CONTACT. Provide the organization or individual(s) name with corresponding contact information who will be included in the published citation as the point of contact and will respond to external questions about the content of the STI product.

Part II. STI PRODUCT MEDIA/FORMAT AND LOCATION/ TRANSMISSION (To be completed by recipient/contractor)

A. MEDIA/FORMAT INFORMATION

1. **Medium**. This is a required field. Select one of the medium options provided. Note: When announcement record only is submitted, select "No full-text."

2. **Size of STI Product**. Provide the total number of pages or other designation which gives an indication of the size of the information product (e.g., 200 pages; 20 images; 3500 kilobytes; 3-3 1/2 inch diskettes).

3. **File Format**. This is a required field if the STI product is electronic full-text. Select one of the options provided.

4. **If Computer Medium or Audiovisual Material** (do not include software packages).

a. Indicate the quantity and type of medium, e.g., 2 videocassettes, 1 magnetic tape.

b. Indicate the machine with which the medium is compatible, i.e., with which it can be used (e.g., VHS; IBM PC compatible, hard disk, 8 Megs.)

c. Enter any other information which would be helpful to the user of the STI product (e.g., programming language, file format, etc.)

B. LOCATION/TRANSMISSION INFORMATION

STI PRODUCT IS BEING TRANSMITTED:

1. This is a required field. Provide if the full-text STI product is being transmitted electronically. Indicate if product is being transmitted via Internet-accessible system called Elink at https://www.osti.gov/elink/.

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Part III: STI PRODUCT REVIEW/RELEASE INFORMATION (To be completed by DOE)

A. STI PRODUCT REPORTING REQUIREMENT REVIEW

1. This is a required field if all other required STI products have been received for this award by OSTI and this STI product is the final deliverable required according to the technical information reporting requirement.

2. Indicated if the STI product is not suitable for dissemination beyond DOE based on report type or content, it is being submitted because it fulfills a technical information reporting requirement.

B. RELEASEING OFFICIAL - This is a required field. Provide the name and additional information of the site's individual(s) responsible for the appropriate review and release of the STI product. Do not forward this form or the STI product until after it has been reviewed and released for announcement.

OMB BURDEN DISCLOSURE STATEMENT

Public reporting burden for this collection of information is estimated to average 30 minutes per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to the Office of Information, Records and Resource Management, SO-31, FORS, U.S. Department of Energy, Washington, DC 20585 and to the Office of Management and Budget (OMB), Paperwork Reduction Project (1910-1400), Washington, D.C. 20503.