

MEMO

To: Sabbatical Leave Committee

From Dr. Alexei Iretski

Date: November 15, 2016

Subject: Sabbatical Leave Application Fall 2017 –Spring 2018

Expanding National and International Research Collaboration on Design and Study of Novel Transition Metal Containing Catalysts for Small Molecules Activation. Physical Chemistry Curriculum Improvement.

Please find enclosed my sabbatical leave application for the academic year 2017-2018. It includes a cover page, a proposal, a resume, copies of the front pages of the published papers and patents upon which this proposal is based, and letters of invitation and acceptance from Prof. Peter C. Ford (University of California, Santa Barbara), Dr. Tigran Kurtikyan (Molecule Structure Research Center of the Scientific-Technological Center of Organic and Pharmaceutical Chemistry, National Academy of Sciences, Yerevan, Republic of Armenia), and Dr. Jörg Spengler (Interkat Katalysatoren GmbH, Königswinter, Germany).

Provost Office

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Lake Superior State University

**Expanding National and International Research Collaboration on
Design and Study of Novel Transition Metal Containing Catalysts
for Small Molecules Activation. Physical Chemistry Curriculum
Improvement.**

Sabbatical Leave Proposal Application Fall 2017–Spring 2018

Submitted by

Dr. Alexei Iretski

November 15, 2016

Introduction

The research part of a sabbatical proposal focuses on activation of small molecules, including their activation under biological conditions. I am familiar with these topics of research due to my background in the area of computational, inorganic and material chemistry and my involvement in collaborative research with University of California Santa Barbara (UCSB) and the Molecule Structure Research Center of the National Academy of Sciences, Republic of Armenia. This sabbatical will help to strengthen these collaborations, further promote undergraduate research at LSSU, and raise the profile and publicize the institution as a whole. In addition I plan to establish an international collaboration with a research division of Interkat, GmbH. (Germany) as I am invited to spend part of my sabbatical there. Ideally I plan to work for up to 3 months at each location. Specifically, I am proposing: 1) to work on design of a Porous Metal Oxides formulation for catalytic conversion of exhaust gases from gasoline, diesel, and compressed natural gas engines; 2) to study the conditions of photochemical or thermal release of biologically important small molecules from metal complexes; 3) to lay a foundation for more advanced undergraduate student research at LSSU.

The curriculum development part of this application has a goal of producing a suitable laboratory manual for CHEM363 Kinetics and Reaction Dynamics class which is an integral part of our department's American Chemical Society (ACS) approved degree in Chemistry and Biochemistry. I plan to work on the lab manual during the remaining 3 months of the year.

The successful completion of the proposed activities will provide the basis to seek external funding, improve the chemistry instructions and promote our program as one of the best places to study chemistry at the undergraduate level.

Background

Much of my current research is focused on a design of novel solid base catalysts based on modified hydrotalcite-like materials and use of computational chemistry to predict and/or explain the properties of biologically relevant NO and CO bearing complexes. My previous work¹ on reversible carbon dioxide (CO₂) adsorbent resulted in support from the NSF funded program PIRE-ECCI (Partnership for International Research and Education – Electron Chemistry and Catalysis at Interfaces)² and my recognition as collaborator for the NSF Chemical Bonding Center CENTC (Center for Enabling New Technologies Trough Catalysis)³ and Center for Sustainable Use of Renewable Feedstocks⁴ - Phase I NSF Center for Chemical Innovation, funded by the NSF Division of Chemistry since September 2012. This work led to a new patented technology for converting lignins into

¹ M. G. White, A. V. Iretski, J. S. Weigel, R. L. Chang, and J. R. Brzozowski. Adsorbents, Methods of Preparation, and Methods of Use Thereof. Patent US 7,442,232 B2 (28 October 2008).

² <http://pire-ecci.ucsb.edu/>

³ <http://www.nsfcentc.org/>

⁴ <http://censurf.chem.ucsb.edu/>

liquid fuels⁵. This type of polymetallic porous oxides catalysts also has a potential application in the treatment of exhaust gases from gasoline, diesel and compressed natural gas engines. Details of the catalytic research constitute Specific Aims I.

In the last few years I took part in a computational and experimental research on NO release in biological conditions by transition metal nitrosyl complexes^{6,7,8}. Nitric oxide (nitrogen monoxide, NO) is an bioregulator that has important roles in mammalian physiological functions such as vasodilation, inflammation, neuronal transmission, and immune system response. I plan using some of my sabbatical to continue the investigation of photochemical NO release from porphyrin and related metal nitrosyl complexes. This is Specific Aim II.

Since the introduction of the CHEM363 laboratory class the instructors were struggling with offering of suitable experimental work for our students. This class is required for all B.S. Chemistry students, and the students majoring in Biochemistry, Forensic Chemistry and Environmental Chemistry, as directed by the ACS. In the past few years I adapted several experimental procedures judged to be feasible in our laboratories and I will take time to combine them in one convenient place – the laboratory manual. This is Specific Aim III.

Proposed Research and Specific Aims

a) Novel Porous Metal Oxides Catalysts

The development of new, efficient, heterogeneous catalysts for a biomass conversion into liquid fuels represents one of the major challenges for chemistry and chemical engineering today. As the gasoline and diesel prices were increasing significantly over last few years, a more innovative approach is required to alleviate the energy supply problem. One way to address it, along with better use of solar and wind energy, is to turn attention to renewable energy sources – biomass. Specifically, the lignocellulosic biomass is a renewable source of energy if converted into liquid fuel or depolymerized into the aromatic monomers. In cooperation with Prof. P. Ford (UCSB) we have already developed a promising catalyst for biodiesel production from seed oil, and for deconstruction (solvolysis) of ornosolv lignins. Lignins, that constitute up to 30% of wood biomass and consist mostly of propanephenol polymers, are readily

⁵ T. D. Matson, P. C. Ford, G. Macala, and A. Iretski. Process For Direct Conversion Of Biomass To Liquid Fuels And Chemicals. US 8786494, The Regents of the University of California, USA (08-05-2014).

⁶ A. D. Ostrowski, R. O. Absalonson, M. A. De Leo, G. Wu, J. G. Pavlovich, J. Adamson, B. Azhar, A. V. Iretskii, I. L. Megson, and P. C. Ford. Photochemistry of *trans*-Cr(cyclam)(ONO)₂⁺, a Nitric Oxide Precursor. *Inorg. Chem.*, **50**, 4453 (2011).

⁷ J. C. M. Pereira, A. V. Iretskii, R.-M. Han, and P. C. Ford. Dinitrosyl Iron Complexes with Cysteine. Kinetics Studies of the Formation and Reactions of DNICs in Aqueous Solution. *J. Am. Chem. Soc.*, **137**, 328 (2015).

⁸ T. S. Kurtikyan, V. A. Hayrapetyan, G. G. Martirosyan, R. K. Ghazaryan, A. V. Iretskii, H. Zhao, K. Pierloot, and P. C. Ford. Nitrosyl isomerism in amorphous Mn(TPP)(NO) solids. *Chem. Comm.*, 12088 (2012).

available as a waste product from paper industry and bioethanol plants but have limited or no use as energy resource today, except for a boiler fuel. Degradation of lignin is achieved predominantly through a hydrogenolysis, either under 40 atm H₂ pressure, or using a base catalysed depolymerization (BCD) at high temperature in near critical water or supercritical alcohols. I plan to further contribute to this research during my visit to UCSB laboratories. In addition, continuous collaboration with UCSB has also provided the opportunity to LSSU students to complete a summer internship in Santa Barbara, CA. Since the summer of 2005 several LSSU chemistry students (N. Braschayko'06, S. Kern'06, K. Darling'07, A. Robertson'08 –twice, C. Johnson'09, M. Fettig'10, D. Hamann'15, J. Peterson'16, and G. Hubbell'17) took advantage of this opportunity to experience a feeling of a graduate school as well as learn valuable research skills. I wish to continue the offering of such internships to LSSU students in the future.

Interestingly, the automotive industry can also benefit in potential use of our PMO based catalysts to clean the exhaust gases of various types of combustion engines. Several conversations with Dr. Jörg Spengler, Managing Director of Interkat Katalysatoren GmbH, resulted in an invitation to work in Germany for at least 3 months and try to substitute the current generation of perovskite-based catalysts for our proprietary hydrotalcite-based formulations. The main goal of the project is to evaluate the suitability of modified PMOs to use with compressed natural gas engines. The idea is to synthesize the Al-Mg hydrotalcite-like materials that will contain 5-10% of rare earth elements and/or platinum metals. Upon calcination these precursors develop high surface area (required for any heterogeneous process) and are extremely stable with regard to sintering. Preliminary work has demonstrated the significant activity, however much further research is required in order to obtain a working prototype that is imperishable in presence of various impurities, most important unfaltering to sulfur.

Further development of PMO-based catalysts constitutes the specific aim I.

b) Photochemical release of nitric oxide and carbon monoxide.

My earlier collaboration with Prof. T. Kurtikyan (Armenian Academy of Science) suggested some new pathways in photoactivation of nitrosyl and nitrosyl nitrite complexes of Co, Mn, and Fe in biological conditions using low energy skin penetrating near-infrared radiation by means of two-photon excitation. Nitric oxide has several well-established roles in mammalian biology closely tied to its interactions with metalloproteins, especially heme proteins. I plan to continue this work during a part of sabbatical leave in Yerevan (Armenia) using metal porphyrins as a model using a unique low-temperature high vacuum IR spectrometer that allow to obtain and study thin films of such compounds.

In addition, with Prof. P. Ford (UCSB) we just started collaborative efforts to find suitable conditions for carbon monoxide (CO) release from polycarbonyl dimetallic complexes upon excitation by light. Carbon monoxide is a normal neurotransmitter as well as one of three gases that naturally modulate inflammatory responses in the body (the other two being nitric oxide and hydrogen sulfide), and has received a great deal of

clinical attention as a biological regulator. This work will be done during a visit to UCSB (Santa Barbara, CA).

Studies of photochemical and thermal activation of NO and CO complexes constitute specific aim II.

c) Improvements in Undergraduate Education in Chemistry.

Our laboratory class CHEM363 Kinetics and Reaction Dynamics was introduced a few years ago as part of the curriculum improvement when our department was seeking the approval of the American Chemical Society of our B.S. Chemistry degree. Last year during the preparations for the re-accreditation by the ACS our department expanded the reach of the class to all the students majoring in chemistry related degrees.

The different educational needs for the B.S. chemists and, say, B.S. biochemists or B.S. forensic chemists are evident and require the individual approach for the students within the same class. The students majoring in different flavors of Chemistry have unlike level of preparedness and of learning outcomes. B.S. Chemistry degree requires in depth understanding of mechanisms of chemical reactions and the ways of elucidating these mechanisms that are based upon kinetic measurements. The students in other sub-disciplines often need only hands-on practice in determining the rate laws and activation parameters of the reactions. The challenge, therefore, is to offer different experience to variety of students within the same laboratory settings.

Currently there is no laboratory manual for such course. Initially we did use an eclectic mix mostly of General Chemistry laboratories with significantly increased demands for accuracy of measurements. Not only the choice of presented in laboratory format experiments is extremely limited (to 3, to be precise), but also they all explore the same convenient oxidation-reduction core reaction with some derivations in reagents and reaction conditions. This is clearly insufficient for the semester long class. Over the years I identified some suitable experiments that were described in Journal of Chemical Education and online as part of Massachusetts Institute of Technology open access courses at <https://ocw.mit.edu>. The challenge consists of adapting those laboratories to our facilities and to present our students with the opportunity to use different instruments to determine the kinetic parameters of the processes in somewhat closed to industrial or advanced laboratory settings.

Our department has recently acquired a new diode-array UV-Vis spectrometer and is in the process of purchasing of the new NMR instrument. Both spectrometers allow for a precise temperature control and both can be used to follow the chemical kinetics. My goal is to fully incorporate UV-Vis and NMR spectrometry into our CHEM363 class.

As a part of this sabbatical application I propose to combine all the tested in our laboratories experiments in one student manual. This work will require further adaption of published procedures in order to use the available instrumentation and present them in a way that will allow for diversity of experiences and learning outcomes for different student needs. For example, B.S Chemistry students will thoroughly elucidate the reaction mechanism in a study that requires up to 5 laboratory periods. At the same time the simple determination of reaction rate and/or activation parameters can be successfully

completed in only 1-2 laboratory periods using the same instrumentation. This type of study is more suitable for B.S Forensic Chemistry students or B.S. Biochemistry students.

Preparation of laboratory manual for CHEM363 class constitutes specific aim III.

II. Sabbatical Benefits

The proposed sabbatical will benefit the Department of Chemistry and Environmental Sciences, the University, and me. Personal benefits will result in published work in peer-review journals and/or a conference presentation. The proposed research strongly enforces the existing scientific relationship between the LSSU, UCSB, and Armenian Academy of Science. Successful completion of sabbatical will also help to offer our students better post graduate opportunities. An anticipated improvement in our Physical Chemistry curriculum will help in better preparation the chemistry students.

My participation in solid base catalyst research and in NO laser-controlled release has brought national and international acclaim to Lake Superior State University and this sabbatical will further highlight the university and help in establishing itself as a unique and premier undergraduate institution. In brief, just as LSSU mission statement declares, this sabbatical leave will *serve the regional, state, national and global communities by contributing to the growth, dissemination, and application of knowledge.*

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Prepared: November, 2016

EDUCATION

Ph.D. in Inorganic Chemistry

Institute of Technology, Saint Petersburg, Russia. 1984.

Dissertation: "Coordination chemistry and reactivity of some rhodium complexes with nitrogen and sulfur containing ligands".

M.S. in Radiation Chemistry

Institute of Technology, Saint Petersburg, Russia. 1981

Thesis: "Synthesis and transformations of gold complexes with nitrogen containing ligands".

WORK EXPERIENCE

Lake Superior State University, Sault Sainte Marie, MI:

Professor with Tenure – Life Chemistry I CHEM 104 (3 credits), General Chemistry I CHEM 115 (5 credits) and General Chemistry II CHEM 116 (5 credits) both with laboratories, Survey of Organic Chemistry CHEM 220 (3 credits) with laboratory, Inorganic Chemistry CHEM261 (3 credits) with laboratory, Physical Chemistry I (Thermodynamics) CHEM361 (3 credits), Physical Chemistry II (Quantum Chemistry) CHEM 362 (3 credits), Physical Chemistry Laboratory (Kinetics and Reaction Dynamics) CHEM363 (1 credit), Advanced Inorganic Chemistry CHEM 461 (3 Credits), and Advanced Inorganic Chemistry Laboratory CHEM 462 (1 credit).

2002 – present

Visiting Professor – Advanced Inorganic Chemistry (Chem173A / 268A).
Summers 2005-2009, 2011-2016.

Mississippi State University, Mississippi State, MS 39762:

Visiting Research Professor at Dave C. Swalm School of Chemical Engineering.
Biomass conversion into fuel. (sabbatical leave).

September 2009 – August 2010

Pierre and Marie Curie University, Paris, France

Visiting Research Professor at Laboratory of Surface Reactivity. Solid bases from
modified hydrotalcites (sabbatical leave)

November - December 2009

Institute of Technology, Saint Petersburg, Russia:

Assistant Professor – General and Inorganic Chemistry. Coordination Chemistry.
Qualitative Analysis.

1989-1996

Adjunct Instructor – General and Inorganic Chemistry. Coordination Chemistry.
Qualitative Analysis.

1984-1989

Teaching Assistant – General and Inorganic Chemistry.

1982-1983.

Research Associate, Georgia Institute of Technology, Atlanta, GA, 1998 – 2002 (with Prof. M.G.White).

Isomerization of alkyl-aromatics in superacidic media. Selective side-chain oxidation of alkyl-benzenes over a palladium catalyst. Oxidative coupling of cycloalkanes in superacidic media. Hydrotalcite-like materials as advanced CO₂-adsorbents. Heterogeneous catalysis – methane partial oxidation, autothermal reforming.

Research Associate, University of Sheffield , Sheffield, UK, 1996 –1998 (with Prof. P.M.Maitlis).

Platinum complexes in hydrodesulfurization.

Postdoctoral Researcher, University of Sheffield , Sheffield, UK, 1995 –1996 (with Prof. P.M.Maitlis).

Platinum complexes in hydrodesulfurization.

Research Associate, Coordination Chemistry Laboratory, Toulouse, France, 1993-1994 (with Prof. R.Poilblanc).

Complexes of rhodium with diphenylphosphinocyclopentadienyl as ligand.

Postdoctoral Researcher, University of Paris-Sud, Orsay, France, 1992 (with prof. H.B.Kagan).

Chiral aminosulfoxides as the ligands of asymmetric rhodium catalysts in the hydrogenation and hydrosilylation reactions.

Staff Scientist, Institute of Technology, Saint Petersburg, Russia, 1984-1989.
Coordination chemistry of rhodium and platinum.

LANGUAGES

Russian – native language; English and French – fluent

Papers

1. A. O. Razgoniaev, E. V. Butaeva, A. V. Iretskii, and A. D. Ostrowski. Changing Mechanical Strength in Cr(III)-Metallosupramolecular Polymers with Ligand Groups and Light Irradiation. *Inorg. Chem.* **55**, 5430 (2016).
2. J. C. M. Pereira, A. V. Iretskii, R.-M. Han, and P. C. Ford. Dinitrosyl Iron Complexes with Cysteine. Kinetics Studies of the Formation and Reactions of DNICs in Aqueous Solution. *J. Am. Chem. Soc.* **137**, 328 (2015).
3. J. L. Heinecke, C. Khin, J. C. M. Pereira, S. A. Suarez, A. V. Iretskii, F. Doctorovich, and P. C. Ford. Nitrite Reduction Mediated by Heme Models. Routes to NO and HNO? *J. Am. Chem. Soc.* **135**, 4007 (2013).
4. G. G. Martirosyan, T. S. Kurtikyan, A. S. Azizyan, A. V. Iretskii, and P. C. Ford. Weak coordination of neutral S- and O-donor proximal ligands to a ferrous porphyrin nitrosyl. Characterization of 6-coordinate complexes at low T. *J. Inorg. Biochem.* **121**, 129 (2013).
5. T. S. Kurtikyan, V. A. Hayrapetyan, G. G. Martirosyan, R. K. Ghazaryan, A. V. Iretskii, H. Zhao, K. Pierloot, and P. C. Ford. Nitrosyl isomerism in amorphous Mn(TPP)(NO) solids. *Chem. Comm.* 12088 (2012).
6. T. D. Matson, K. Barta, A. V. Iretskii, and P. C. Ford. One-Pot Catalytic Conversion of Cellulose and of Woody Biomass Solids to Liquid Fuels. *J. Am. Chem. Soc.* **133**, 14090 (2011).
7. D. F. Zigler, E. Torbin, G. Wu, A. Iretskii, E. Cariati, and P. C. Ford. Mononuclear copper(I) complexes of *O*-*t*-butyl-1,1-dithiooxalate and *O*-*t*-butyl-1-perthio-1-thiooxalate. *Inorg. Chim. Acta*, **374**, 261 (2011).
8. A. D. Ostrowski, R. O. Absalonsen, M. A. De Leo, G. Wu, J. G. Pavlovich, J. Adamson, B. Azhar, A. V. Iretskii, I. L. Megson, and P. C. Ford. Photochemistry of *trans*-Cr(cyclam)(ONO)₂⁺, a Nitric Oxide Precursor. *Inorg. Chem.* **50**, 4453 (2011).
9. K. Barta, T. D. Matson, M. L. Fettig, S. L. Scott, A. V. Iretskii, and P. C. Ford. Catalytic disassembly of an organosolv lignin *via* hydrogen transfer from supercritical methanol. *Green Chem.* **12**, 1640 (2010).
10. T. S. Kurtikyan, A. A. Hovhannisyan, A. V. Iretskii and P. C. Ford. Six-Coordinate Nitro Complexes of Iron(III) Porphyrins with *trans* S-Donor Ligands. Oxo-Transfer Reactivity in the Solid State. *Inorg. Chem.*, **48**, 11236 (2009).
11. T. S. Kurtikyan, A. A. Hovhannisyan, A. Iretskii and P. C. Ford. Reaction of the Five-Coordinate O-Nitrito Complex Fe(Por)(ONO) (Por=*meso*-tetra-arylporphyrinato) with THF Gives Two Six-Coordinate Isomers. *Aust. J. Chem.*, **62**, 1226 (2009).
12. C. T. Yavuz, B. D. Shinall, A. V. Iretskii, M. G. White, T. Golden, M. Atilhan, P. C. Ford, and G. D. Stucky. Markedly Improved CO₂ Capture Efficiency and Stability of Gallium Substituted Hydrotalcites at Elevated Temperatures. *Chem. Mater.*, **21**, 3743 (2009).
13. G. S. Macala, T. D. Matson, C. L. Johnson, R. S. Lewis, A. V. Iretskii, and P. C. Ford. Hydrogen Transfer from Supercritical Methanol over a Solid Base Catalyst: A Model for Lignin Depolymerization. *ChemSusChem.*, **2**, 215 (2009).
14. G. S. Macala, A. W. Robertson, C. L. Johnson, Z. B. Day, R. S. Lewis, M. G. White, A. V. Iretskii, and P. C. Ford. Transesterification Catalyst From Iron Doped Hydrotalcite-like Precursors: Solid Bases for Biodiesel Production. *Catal. Lett.*, **122**, 205 (2008).

15. C. Khin, M. D. Lim, K. Tsuge, A. Iretskii, G. Wu, and P. C. Ford. Amine Nitrosation via NO Reduction of the Polyamine Copper(II) Complex $\text{Cu}(\text{DAC})^{2+}$. *Inorg. Chem.*, **46**, 9323 (2007).
16. T. S. Kurtikyan, A. A. Hovhannisyanyan, M. E. Hakobyan, J. C. Patterson, A. Iretskii, and Peter C. Ford. Reactions of Nitrogen Oxides with the Five-Coordinate Fe^{III} (porphyrin) Nitrito Intermediate $\text{Fe}(\text{Por})(\text{ONO})$ in Sublimed Solids. *J. Amer. Chem. Soc.*, **129**, 3576 (2007).
17. C. A. Joseph, M. S. Lee, A. V. Iretskii, G. Wu, and P. C. Ford. Substituent Effects on Nitrosyl Iron Corrole Complexes $\text{Fe}(\text{Ar}_3\text{C})(\text{NO})$. *Inorg. Chem.*, **45**, 2075 (2006).
18. M. Volpe, G. Wu, A. Iretskii, and P. C. Ford. Photochemical and Time Resolved Spectroscopic Studies of Intermediates Relevant to Iridium-Catalyzed Methanol Carbonylation: Photoinduced CO Migratory Insertion, *Inorg. Chem.*, **45**, 1861 (2006).
19. A. V. Iretskii, S. C. Sherman, E. J. Angueira, and Mark G. White, "Arene Formylation in Perfluoroalkanesulfonic Acids", Leading Edge Catalysis Research, edited by Lawrence P. Bevy, Nova Science Publications, Inc., New York, (2005).
20. J. L. Gole, A. V. Iretskii, M. G. White, A. Jacob, W. B. Carter, S. M. Prokes, and Ann S. Erickson, "Suggested Oxidation State Dependence for the Activity of Submicron Structures Prepared from Tin/Tin Oxide Mixtures", *Chem. Mater.*, **16**, 5473 (2004).
21. J. L. Gole, B. D. Shinall, A. V. Iretskii, M. G. White, and Ann S. Erickson. "Surface Oxidation States in Si/SiO₂ Nanostructures Prepared from Si/SiO₂ Mixtures". *Langmuir*, **20**, 260 (2004)
22. J. L. Gole, B. D. Shinall, A. V. Iretskii, M. G. White, W. B. Carter, and Ann S. Erickson, "Tunable Surface Oxidation States in Si/SiO₂ Nanostructures Prepared from Silicon/Silica Mixtures", *ChemPhysChem*, **4**, 1016 (2003)
23. S. C. Sherman, A. V. Iretskii, M. G. White, C. Gumienny, L. M. Tolbert, and D. A. Schiraldi. "Isomerization of Substituted Biphenyls by Superacid. A Remarkable Confluence of Experiment and Theory.", *J. Org. Chem.*, **67**, 2034 (2002).
24. A. V. Iretskii, S. C. Sherman, and M. G. White. "New Coupling and Isomerization Reactions Catalyzed by a Protic Superacid", In *Chemical industries*, v. **82: Catalysis of organic reactions. Ed. Ford, M. E. Marcel Dekker: New York, 181 (2001).**
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26. S. D. George, S. C. Sherman, A. V. Iretskii, and M. G. White. "Direct Liquid-Phase Side-Chain Oxidation of Alkylbenzenes Over $[\text{Pd}(\text{Phen})(\text{OAc})_2]$ Catalyst", *Catal. Lett.*, **65**, 181 (2000).
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31. A. Iretskii, J. J. Garcia, G. Picazo, and P. M. Maitlis. "A Key Intermediate in the Platinum-Mediated Hydrodesulfurization of Dibenzothiophene", *Catal. Lett.*, **51**, 129 (1998).

- Chem. Comm.*, 61 (1998).
33. A. V. Iretskii and H. B. Kagan. "Rhodium(I) Cation Complexes With (R)-(+)-2-[(4-Methylphenyl)Sulfinylmethyl] PIPRIDINE", *Zh. Obshch. Khim.*, **67**, 353 (1997).
 34. A. Iretskii, M. C. Jennings, and R. Poilblanc. "Transition-Metal Derivatives of the Cyclopentadienylphosphine Ligands. 11. Reactivity of the Dinuclear Bridged Rhodium(II) Complexes Toward Nitrogen-Containing Ligands", *Inorg. Chem.*, **35**, 1266 (1996).
 35. O. B. Zhidkova, A. V. Iretskii, N. K. Skvortsov, E. V. Kopylova, N. N. Labeish, and V. A. Galishev. "Interaction of [RhCO(Ph₂PNCO)₂Cl] Complex With Alcohols", *Zh. Obshch. Khim.*, **66**, 1078 (1996).
 36. O. B. Zhidkova, T. S. Dolgushina, N. N. Labeish, V. K. Belskii, V. A. Galishev, and A. V. Iretskii. "Diphenylphosphinic Rhodium(I) Complexes in Attachment Reactions", *Zh. Obshch. Khim.*, **65**, 769 (1995).
 37. A. V. Iretskii, O. B. Zhidkova, T. S. Dolgushina, N. N. Labeish, N. A. Lasitsa, N. K. Skvortsov, and V. A. Galishev. "Aminophosphine Complexes of Rhodium(I) and Their Catalytic Activity in Reactions of Hydroxylation", *Zh. Obshch. Khim.*, **63**, 1681 (1993).
 38. A. V. Iretskii, T. S. Rosyanova, and L. I. Danilina. "Hydrogen-Chloride Interaction With Rhodium(I) [RhCO(Ph₂CH₂CH₂CN)₂Cl] Complex", *Koord. Khim.*, **19**, 564 (1993).
 39. A. V. Iretskii, O. B. Zhidkova, and V. N. Demidov. "Platinum(II) and Rhodium(I) Complexes [PtPhenACl][Rh(CO)₂Cl₂]", *Zh. Neorg. Khim.*, **36**, 1185 (1991).
 40. A. V. Iretskii, T. S. Rosyanova, and L. I. Danilina. "Rhodium Complexes With 2-Cyanoethyldiphenylphosphine", *Koord. Khim.*, **17**, 1110 (1991).
 41. A. V. Iretskii, M. L. Petrov, Yu. N. Kukushkin, E. B. Shamuratov, A. S. Batsanov, and Yu. T. Struchkov. "Rhodium(I) Carbonyl Chloride Complexes With Derivatives of 1,2,3-Thiadiazole and 1,2,3-Selenadiazole. Synthesis and the X-Ray Crystal Structure", *Metallorg. Khim.*, **4**, 1314 (1991).
 42. A. V. Iretskii, T. S. Dolgushina, N. N. Labeish, and V. A. Galishev. "Rhodium(I) Complexes With Trivalent Phosphorus Acid Isocyanates", *Zh. Obshch. Khim.*, **61**, 2777 (1991).
 43. L. I. Danilina, A. V. Iretskii, and T. S. Rosyanova. "Rhodium(I) Carbonyl Tris-(2-Cyanoethyl)Phosphine Complexes", *Koord. Khim.*, **16**, 1390 (1990).
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US008796494B2

(12) **United States Patent**
Matson et al.

(10) Patent No.: **US 8,796,494 B2**

(45) Date of Patent: **Aug. 5, 2014**

(54) **PROCESS FOR DIRECT CONVERSION OF BIOMASS TO LIQUID FUELS AND CHEMICALS**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 992 days.

(21) Appl. No.: **12/885,397**

(22) Filed: **Sep. 17, 2010**

(65) **Prior Publication Data**
US 2011/0065814 A1 Mar. 17, 2011

Related U.S. Application Data

(60) Provisional application No. 61/243,343, filed on Sep. 17, 2009.

(51) Int. Cl.
C07C 1/00 (2006.01)
C10L 1/00 (2006.01)

(52) U.S. Cl.
USPC 585/240; 585/242; 585/14; 44/307;
44/606; 44/605

(58) **Field of Classification Search**
USPC 585/240, 242, 14, 44/605, 606, 307;
554/141, 170

See application file for complete search history.

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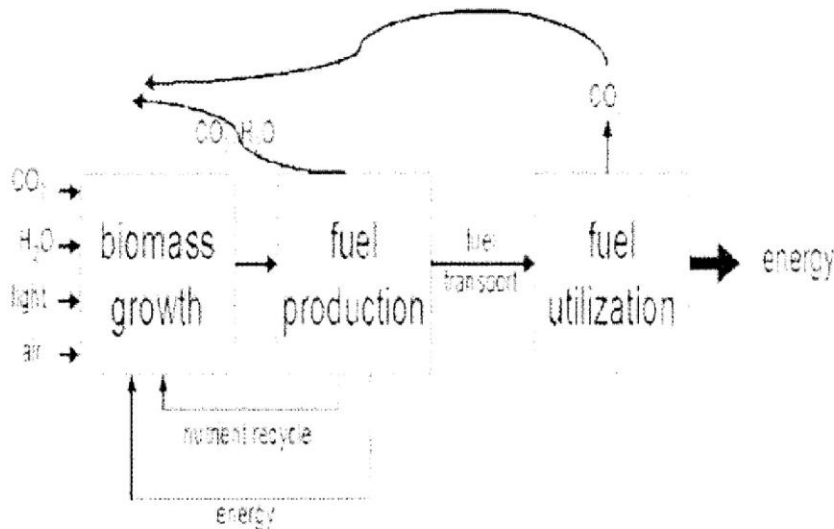
(Continued)

Primary Examiner: Nima Bhat
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(57) **ABSTRACT**

A method of catalytically preparing a fluid product from solid carbonaceous material is described. In the method, at least one of the following equilibria is established by one or more catalysts: a) $\text{CH}_2\text{OH}-\text{CO}+2\text{H}_2$, b) $\text{CO}+\text{H}_2\text{O}-\text{CO}_2+\text{H}_2$. In some versions, the solid carbonaceous material is woody biomass. Components of the fluid product can include one or a combination of C_2-C_4 alcohols. In certain versions, the method can be practiced with substantially all of the carbon in the carbonaceous material being converted to the fluid product. Also, in some versions, the fluid product can be prepared with substantially no char formation. The fluid product of various versions can be used directly as fuel or as a reagent for preparing commodity chemicals without the need for separating the fluid product components.

24 Claims, 3 Drawing Sheets





US007442232B2

(12) **United States Patent**
White et al.(10) **Patent No.:** US 7,442,232 B2
(45) **Date of Patent:** Oct. 28, 2008(54) **ADSORBENTS, METHODS OF
PREPARATION, AND METHODS OF USE
THEREOF**(75) Inventors: **Mark G. White**, Woodstock, GA (US);
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Atlanta, GA (US)(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 443 days.(21) Appl. No.: **10/518,188**(22) PCT Filed: **Jun. 19, 2003**(86) PCT No.: **PCT/US03/19290**§ 371 (c)(1),
(2), (4) Date: **Jan. 18, 2006**(87) PCT Pub. No.: **WO04/000440**PCT Pub. Date: **Dec. 31, 2003**(65) **Prior Publication Data**

US 2006/0144227 A1 Jul. 6, 2006

Related U.S. Application Data(60) Provisional application No. 60/390,050, filed on Jun.
19, 2002, provisional application No. 60/449,689,
filed on Feb. 24, 2003.(51) **Int. Cl.**
B01D 53/04 (2006.01)(52) **U.S. Cl.** **95/96; 95/139; 95/900;**
423/230; 502/56; 502/103(58) **Field of Classification Search** **95/96;**
95/106, 115, 118-120, 126, 139, 900; 423/230;
502/34, 56, 102, 103, 414

See application file for complete search history.

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Primary Examiner—Frank M Lawrence(74) *Attorney, Agent, or Firm*—Thomas, Kayden,
Horstemeyer & Risley, LLP(57) **ABSTRACT**Adsorbents and methods of use thereof are provided. One
representative, among others, includes an adsorbent having
an alkali metal promoted, mixed trivalent layered double
hydroxide (LDH) composition. When the mixed trivalent
layered double hydroxide (LDH) composition is heated to a
temperature ranging from about 300° C. to 450° C., an the
adsorbent having an adsorption capacity of at least 0.8 milli-
moles of CO₂ adsorbed per gram of adsorbent is formed.**20 Claims, 1 Drawing Sheet**

Dinitrosyl Iron Complexes with Cysteine. Kinetics Studies of the Formation and Reactions of DNICs in Aqueous Solution

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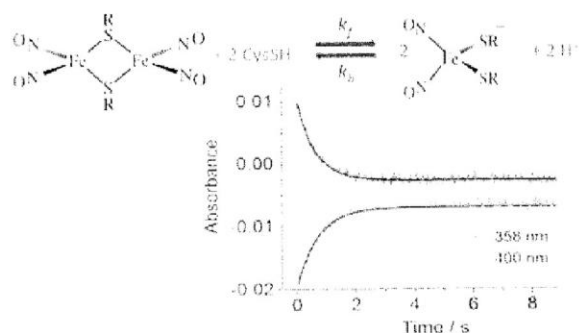
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S Supporting Information

ABSTRACT: Kinetics studies provide mechanistic insight regarding the formation of dinitrosyl iron complexes (DNICs) now viewed as playing important roles in the mammalian chemical biology of the ubiquitous bioregulator nitric oxide (NO). Reactions in deaerated aqueous solutions containing FeSO₄, cysteine (CysSH), and NO demonstrate that both the rates and the outcomes are markedly pH dependent. The dinuclear DNIC Fe₂(μ-CysS)₂(NO)₄, a Roussin's red salt ester (Cys-RSE), is formed at pH 5.0 as well as at lower concentrations of cysteine in neutral pH solutions. The mononuclear DNIC Fe(NO)₂(CysS)₂⁻ (Cys-DNIC) is produced from the same three components at pH 10.0 and at higher cysteine concentrations at neutral pH. The kinetics studies suggest that both Cys-RSE and Cys-DNIC are formed via a common intermediate Fe(NO)(CysS)₂⁻. Cys-DNIC and Cys-RSE interconvert, and the rates of this process depend on the cysteine concentration and on the pH. Flash photolysis of the Cys-RSE formed from Fe(II)/NO/cysteine mixtures in anaerobic pH 5.0 solution led to reversible NO dissociation and a rapid, second-order back reaction with a rate constant *k*_{NO} = 6.9 × 10⁷ M⁻¹ s⁻¹. In contrast, photolysis of the mononuclear-DNIC species Cys-DNIC formed from Fe(II)/NO/cysteine mixtures in anaerobic pH 10.0 solution did not labilize NO but instead apparently led to release of the CysS[•] radical. These studies illustrate the complicated reaction dynamics interconnecting the DNIC species and offer a mechanistic model for the key steps leading to these non-heme iron nitrosyl complexes.



INTRODUCTION

Nitric oxide (nitrogen monoxide, NO) is a bioregulator that has important roles in mammalian physiological functions such as vasodilation, inflammation, neuronal transmission, and immune system response.¹ Other NO derivatives, such as S-nitrosothiols (RSNO) and N-nitrosoamines (R₂NNO), heme and non-heme iron nitrosyl complexes as well as the oxidation products, NO₂⁻, ONOO⁻, and NO₃⁻ also have physiological presence, and their specific roles remain the subjects of continuing studies. The dinitrosyl iron complexes (DNICs) comprise one class of such species. DNICs are four-coordinate Fe(NO)₂L₂^{n±} complexes thought to be formed from the chelatable iron pool, thiol-containing ligands (for example, glutathione, cysteine, or protein thiol), and endogenous or exogenous NO.² Although DNICs were first discovered some decades ago,^{3–6} there has been a recent upsurge of interest in the biological or pathological pathways to which these species contribute.^{2,7–15}

Previous studies have demonstrated reversible transformations between the Roussin's red salt ester analogs Fe₂(μ-RS)₂(NO)₄,⁶ which are binuclear DNICs, and mononuclear species [Fe(NO)₂L₂]^{n±} (Figure 1). In aqueous media, these

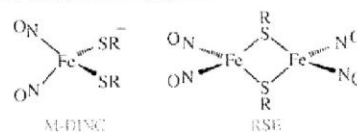


Figure 1. Generic formulas for a mononuclear dinitrosyl iron complex (M-DNIC) (left) and for the binuclear DNIC, a Roussin's red salt ester, (RSE) (right). In the present case, the thiolate RS⁻ is the cysteinate anion, and the M-DNIC Fe(NO)₂(CysS)₂⁻ is designated as Cys-DNIC and the RSE Fe₂(μ-Cys)₂(NO)₄ is designated as Cys-RSE.

Received: October 16, 2014

Published: December 5, 2014

Cite this: *Chem. Commun.*, 2012, **48**, 12088–12090

www.rsc.org/chemcomm

Nitrosyl isomerism in amorphous Mn(TPP)(NO) solids†

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Received 8th October 2012, Accepted 1st November 2012

DOI: 10.1039/c2cc37337h

Reaction of NO with amorphous Mn(TPP) layers gives two Mn(TPP)(NO) isomers with linear and bent Mn–N–O geometries that reversibly interconvert with changes in temperature. DFT computations predict that the linear complex is the singlet ground state while the bent structure is a triplet state.

Metalloporphyrins (MP) remain a focus of attention in the biochemistry of nitric oxide, since many physiological functions of NO involve interactions with heme-proteins.^{1–4} Thus, to derive a better understanding of MP interactions and reactions with various NO_x, we have used IR and optical spectroscopy to probe such species in microporous, solvent free layers of M(TPP).⁵ Here, we describe spectroscopic observations of the NO interaction with amorphous layers of the manganese(II) complex Mn^{II}(TPP) (**1**). This study presents the unexpected observation that the Mn(TPP)(NO) formed is present in two isomeric forms, the relative quantities of which are temperature dependent.

Fig. 1 presents IR spectra of amorphous layers of **1** that have been allowed to react with NO in a vacuum chamber at ambient T (see ESI† for experimental details of the preparation and spectroscopic studies of Mn(TPP)(NO)). Two new strong IR bands at 1739 and 1614 cm⁻¹ appear at frequencies where the $\nu(\text{NO})$ of a coordinated NO might be expected (Fig. 1, dashed line). That both bands are NO stretches was confirmed by the isotopic shifts to 1704 and 1585 cm⁻¹ when ¹⁵NO was used (Fig. 1, dotted line). By contrast, only a single $\nu(\text{NO})$ band was observed for the respective products of analogous NO reactions of Co^{II}(TPP) or Fe^{II}(TPP) layers.^{5a,b}

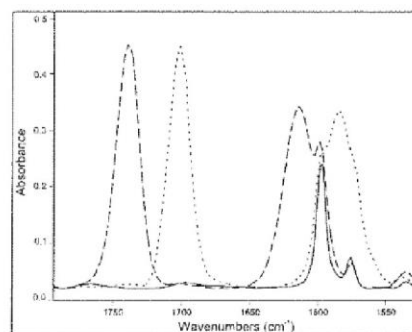


Fig. 1 FTIR spectra of Mn(TPP) (solid line), Mn(TPP)(NO) (dashed line) and Mn(TPP)(¹⁵NO) (dotted line).

There are several possible explanations: (i) formation of a mixture of mono- and di-nitrosyl complexes; (ii) the presence of both 5c Mn(TPP)(NO) and 6c Mn(TPP)(L)(NO) (L = Py or Pip) due to incomplete removal of L in the preparation of the Mn(TPP) layers (see ESI†); (iii) formation of nitrosyl complexes of partially oxidized Mn(TPP); (iv) the presence of two isomeric NO complexes.

With regard to option (i), analogous mono- and di-nitrosyl complexes Fe^{II}(TPP)(NO)_{1,2} have indeed been characterized.⁶ When these are in equilibrium, two $\nu(\text{NO})$ bands are seen: one at 1696 cm⁻¹ (in CHCl₃) for Fe(TPP)(NO)₂ and one at 1681 cm⁻¹ for Fe(TPP)(NO). In the present study, we can assign the $\nu(\text{NO})$ band observed at 1739 cm⁻¹ to mono-nitrosyl Mn(TPP)(NO).^{7,8} Thus, it is unlikely that the 1614 cm⁻¹ band belongs to a di-nitrosyl, since competition between the NOs should decrease the d(Mn) to $\pi^*(\text{NO})$ backbonding and increase $\nu(\text{NO})$ as seen for Fe(TPP)(CO) ($\nu(\text{CO}) = 1973 \text{ cm}^{-1}$) and Fe(TPP)(CO)₂ (2042 cm⁻¹)⁹ and for the di-nitrosyl analog.⁶ Moreover, the relative intensities of the two $\nu(\text{NO})$ bands in Fig. 1 were independent of the quantity of deposited NO, in contrast to the expectation that higher NO loading should favour di-nitrosyl formation.

With regard to (ii), Py and Pip have different σ and π donor and acceptor properties and these differences should be reflected in the $\nu(\text{NO})$ values. However, these frequencies proved to be independent of whether the source of **1** was Mn(TPP)(Py) or Mn(TPP)(Pip). Additionally, the $\Delta\nu(\text{NO})$ between the 5c nitrosyl and 6c mono-nitrosyl Mn(TPP) complexes is generally much smaller than seen here.¹⁰

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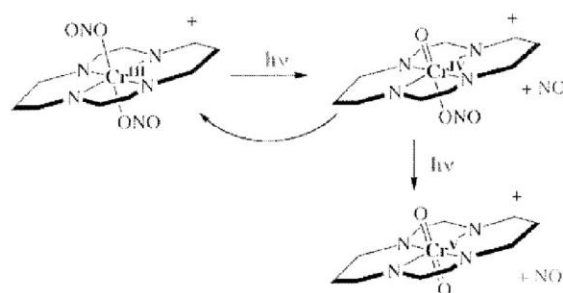
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† Electronic supplementary information (ESI) available: More detailed experimental procedures. Fig. S1: Mn–NO interaction orbital diagrams. Fig. S2: spin density diagram for the triplet bent configuration. Tables S1–S3: calculated energies and other data for isomers and spin states of Mn(P)(NO) and Mn(P)(ON). See DOI: 10.1039/c2cc37337h

Photochemistry of *trans*-Cr(cyclam)(ONO)₂⁺, a Nitric Oxide PrecursorAlexis D. Ostrowski,^{†,||,⊥} Ryan O. Absalonson,^{†,||,⊥} Malcolm A. De Leo,^{†,||,⊥} Guang Wu,[†] James G. Pavlovich,[†] Janet Adamson,[†] Bilal Azhar,[†] Alexei V. Iretskii,[§] Ian L. Megson,[†] and Peter C. Ford^{*,†}[†]Department of Chemistry and Biochemistry, University of California, Santa Barbara, Santa Barbara, California 93106-9510, United States[⊥]Free Radical Research Facility, Department of Diabetes and Cardiovascular Science, University of the Highlands & Islands, Inverness, IV2 3JH, Scotland, U.K.[§]Department of Chemistry & Environmental Sciences, Lake Superior State University, Sault Ste. Marie, Michigan 49783, United States

Supporting Information

ABSTRACT: Experimental and density functional theory (DFT) studies are described that are focused on outlining the reactivity of the known photochemical nitric oxide precursor *trans*-Cr(cyclam)(ONO)₂⁺ ("CrONO", cyclam = 1,4,8,11-tetraazacyclotetradecane). Studies in both aerated and deaerated aqueous media are described as are the roles of both the oxidant O₂ and a reductant such as glutathione in trapping the apparent Cr(IV) photoreaction intermediate *trans*-Cr(cyclam)(O)(ONO)⁺. Also reported and characterized structurally is the Cr(V) product of long-term photolysis in the absence of reducing agents, the *trans*-dioxo species [*trans*-Cr(cyclam)(O)₂](ClO₄). Photosensitization experiments indicate that at least a significant fraction of the reaction occurs from the lowest energy doublet excited state(s). Lastly, cell culture experiments demonstrate that CrONO has little or no acute toxicity either before or after photolysis.



INTRODUCTION

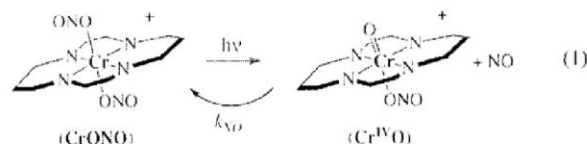
Nitric oxide (also known as nitrogen monoxide) is an endogenous intercellular regulator of numerous physiological processes including vasodilation,¹ some of which are effected at subnanomolar concentrations.² NO also plays key roles in cancer biology and has been implicated in both tumor growth and suppression,³ a dichotomy that is defined by local concentrations, since NO regulation of signaling pathways is both concentration and time-dependent.⁴ There is considerable interest in utilizing direct release of cytotoxic NO concentrations in cancer chemotherapy.^{5,6} However, the complexity and variability of cellular response to NO suggest that such therapeutic applications of NO donors should be concomitant and synergistic with another cytotoxic therapy.^{4a,6a,7} For example, a potentially therapeutic role of NO is as a radiation sensitizer.⁷ Malignant tumors have hypoxic regions that are much more radio-resistant than normoxic tissue, and as a consequence, γ -radiation doses necessary to destroy a malignancy exacerbate collateral damage to surrounding healthy tissue. Hypoxia-induced cell resistance may be alleviated by introducing a radiation sensitizer and/or a vasodilator, and targeted NO delivery at a tumor site would serve both functions.

In these contexts, there has been considerable interest in our laboratory⁸ and others^{9,10} in developing strategies for the release of NO in targeted tissues using excitation with light as the demand signal. A key advantage of photochemical triggering (compared to thermal activation) of appropriate precursors is the precise control that photoexcitation provides regarding the timing,

location, and dosage for administration of a bioactive agent. Such control is essential for effective therapy using nitric oxide.

Transition metal nitrosyl complexes have been attractive photochemical NO precursors in many laboratories owing to their sensitivity to excitation at visible wavelengths. A somewhat different precursor is the chromium(III) dinitrito complex ion, *trans*-Cr(cyclam)(ONO)₂⁺ ("CrONO", cyclam = 1,4,8,11-tetraazacyclotetradecane), which we first reported in 1999 to undergo reversible photoinduced cleavage of the CrO–NO bond¹¹ to give NO plus an intermediate concluded to be a Cr(IV) oxo complex (Cr^{IV}O) as illustrated in eq 1.

We have since described the synthesis of CrONO^{11b} and of several derivatives with pendant chromophores,¹² and demonstrated that excitation of such chromophores was followed by energy transfer to the Cr^{III} center and sensitized photochemistry.^{12,13} We have also further demonstrated



that the NO released by visible range photolysis activates the key enzyme soluble guanylyl cyclase, both in vitro and in coronary

Received: January 16, 2011

Published: April 08, 2011

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November 7, 2016

Dr. Alexei Iretski
Lake Superior State University
650 W. Easterday Avenue
Sault Sainte Marie, MI 49783, USA

Dear Professor Iretski:

On behalf of Department of Chemistry and Biochemistry, I would like to extend you an invitation to be a visiting scholar at University of California, Santa Barbara (UCSB) during part of your sabbatical leave in 2017/18 academic year. We acknowledge that you will receive no monetary remuneration from UCSB, and that you are solely responsible for your financial support throughout your sponsored program. I and other members of my research group are looking forward to collaborating with you on the investigation of photochemical activation of transition metals nitrosyl and carbonyl complexes for the purpose of delivering the small molecule bioregulators NO and CO to physiological targets. Your expertise in DFT calculations of metal complex ground and excited states would be a particularly welcome contribution to our research effort.

Aside from the institutional affiliation with UCSB, we will provide you with laboratory space and office space, computer access, library privileges, and full access to seminars and other functions of the Department of Chemistry and Biochemistry. You will be responsible for your own housing and living arrangements.

Sincerely

A handwritten signature in black ink that reads 'Peter C. Ford'.

Peter C. Ford
Distinguished Professor of Chemistry
UC Santa Barbara

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НАУЧНО-ТЕХНОЛОГИЧЕСКИЙ
ЦЕНТР ОРГАНИЧЕСКОЙ И
ФАРМАЦЕВТИЧЕСКОЙ ХИМИИ
ГНКО

REPUBLIC OF ARMENIA
NATIONAL ACADEMY OF SCIENCES
THE SCIENTIFIC TECHNOLOGICAL CENTER OF
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§ 25 | 10 2016թ.

Dr. Tigran Kurtikyan
Head of Laboratory of Optical Spectroscopy,
Molecule Structure Research Center of the
Scientific-Technological Center of Organic and Pharmaceutical Chemistry,
National Academy of Sciences, Republic of Armenia
26 Azatutyan av., 0014, Yerevan, Armenia

Dr. Alexei Iretski
Lake Superior State University
650 W. Easterday Avenue
Sault Sainte Marie, MI 49783
USA

Dear Dr. Iretski:

I am writing to you to invite you to complete a part of your sabbatical leave in 2016/17 academic year here at the Laboratory of Optical Spectroscopy, Molecule Structure Research Center of the Scientific-Technological Center of Organic and Pharmaceutical Chemistry, National Academy of Sciences, Republic of Armenia. Your duties will include theoretical and experimental research of metal porphyrin complexes that are potential nitric oxide donors upon photoactivation.

Your program supervisor will be Dr. Tigran Kurtikyan. In order for you to have a productive sabbatical leave, we will supply you with several basic necessities. We will supply you with a desk in a shared office space. In addition, you will be supplied with access to my laboratory in this building. Scientific-Technological Center of Organic and Pharmaceutical Chemistry will supply you with a computer account with access to e-mail. I would strongly urge you to bring a newer model of laptop computer with you in order for you to have a better computer to use while you are here. I will also help you locate housing for you before you arrive. I can send you apartment listings or look at apartments for you if you need me to do so.

Please note that you are expected to cover all of your costs, including food, housing, transportation, and travel. We look forward to your arrival and work with us in room #79. Please let me know if you have any questions.

Sincerely,

Prof. Tigran Kurtikyan
Head of Laboratory of Optical Spectroscopy,
Molecule Structure Research Center of the
Scientific-Technological Center of Organic and Pharmaceutical Chemistry,
National Academy of Sciences, Republic of Armenia

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11/8/2016

Dr. Jörg Spengler
INTERKAT Catalyst GmbH
Eduard-Rhein-Straße 25
53639 Königswinter
Germany

Dr. Alexei Iretski
Professor, Department of Chemistry and Environmental Sciences
Lake Superior State University
650 W. Easterday Avenue
Sault Sainte Marie, MI 49783
USA

Dear Dr. Iretski:

I am happy to learn about your desire to do a research and development work in our company during your sabbatical leave in 2017/18 academic year. I am pleased to invite you to complete 3 or more (at your discretion) months of your leave here at Interkat Catalyst GmbH. Your duties will involve the R&D experimental research of polymetallic inorganic catalysts that have are potential industrial application in reducing various engines emissions.

Your program supervisor will be Dr. Jörg Spengler.

In order for you to have a productive sabbatical leave, we will supply you with several basic necessities – the desk in a shared office space, a computer network access, the laboratory space and some common laboratory equipment. I would advise you to bring a newer model of laptop computer.

Please note that you are expected to cover all of your costs, including food, housing, transportation, and travel.

In summary, I invite you to complete a sabbatical leave here at Interkat Catalyst GmbH developing some aspects of emission catalysts. We look forward to your arrival and work with us in Königswinter. Please let me know if you have any questions.

Sincerely,

Dr. Jörg Spengler
Managing Director

INTERKAT Catalyst GmbH