Report on Sabbatical Leave 2017-2018

Dr Alexei Iretski, Department of Chemistry.

As planned, I visited and worked at three different locations: University of California Santa Barbara in Santa Barbara, California; Interkat Katalyzatoren, GmbH in Koenigswinter, Germany and The Scientific Technological Centre of Organic and Pharmaceutical Chemistry in Yerevan, Armenia. While research in Germany was more applied in nature and will take more efforts and time to complete, other work was more rewarding in terms of result.

Keeping up with the purposes for which the leave was granted, this report is organized to address specific aims in my proposal for this sabbatical leave.

A) Novel Porous Metal Oxides Catalysts

Specific aim I.

The main goal of the project was to evaluate the suitability of modified strongly basic PMOs as catalysts for the methane oxidation to use with compressed natural gas engines. The idea was to synthesize the Al-Mg hydrotalcite-like materials that will contain 5-10% of rare earth elements and/or platinum metals. A series of such double layered materias was prepared with various content of Pd, Rh or Pt. Upon calcination these precursors did develop high surface area (required for any heterogeneous process) and were extremely stable with regard to sintering. Regrettably, preliminary tests have demonstrated their lack of significant activity, probably attributed to the presence of strong basic sites, and it was decided to prepare some rather acidic PMOs.

The clays, consisting of Al and Si oxides, were considered as viable model compounds, especially montmorillonite and kaolinite due to the appropriate size of their interlayer space. Various amounts of Pd, Rh, and Pt (from 1 to 3 weight %) were absorbed into the clay structures and upon calcinations the newly generated powders were loaded on the support and tested as catalysts for methane oxidation. All formulations showed excellent adhesion to the support material and were quite active during the tests. In fact, their activity was barely below the activity of the industry benchmark catalyst. Further development is required in order to obtain a working prototype that is imperishable in presence of various impurities, most important unfaltering to sulfur. Therefore this collaboration will be continued.

B) Photochemical release of nitic oxide and carbon monoxide.

Specific aim II.

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. Prof. P. Ford (UCSB) and I continued collaborative efforts to find suitable conditions for carbon monoxide release from polycabonyl dimetallic complexes upon excitation by light. This work was completed during a visit to UCSB (Santa Barbara, CA) and resulted in a publication of a paper[1] in Inorganic Chemistry (an American Chemical Society, ACS, journal) with an impact factor of 4.700. Moreover, this paper was chosen as a cover article for the journal and as an ACS Editors' Choice article. The selection of these articles is based on recommendations by the scientific editors of ACS journals from around the world.

My earlier collaboration with Prof. T. Kurtikyan (Armenian Academy of Science) suggested some new pathways in photoactivation of nitrosyl and nitrosylnitrite 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. This research happened to be much more challenging than anticipated and only recently some encouraging preliminary results were obtained. However, the related research on activation of small molecules like hydrogen sulfide was completed and was presented at two international conferences[2,3] (in Brazil and Armenia) and published as an article[4] in Inorganica Chimica Acta (an Elsevier journal) with an impact factor of 2.264.

C) Improvements in Undergraduate Laboratory Experience

Specific aim III.

Out laboratory class CHEM363 Kinetics and Reaction Dynamics tends to serve the different educational needs of the B.S. chemists and, say, B.S. biochemists or B.S. forensic chemists and require the individual approach for the students within the same class. The challenge, therefore, is to offer different experience to variety of students within the same laboratory settings.

Over the years I identified some suitable experiments described in Journal of Chemical Education on in open online courses and used part of my sabbatical to adapt them to our facilities and test them in the laboratory. Specifically I wanted to emphasize the diversity of the experimental methods that can be used for the determination of the reaction law. Our department has recently acquired a new diode-array UV-Vis spectrometer and the new 400 MHz NMR spectrometer. Both spectrometers allow for a precise temperature control their usage is fully

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[1] Z. Li, A. E. Pierri, P.-J. Huang, G. Wu, A. V. Iretskii, and P. C. Ford. Dinuclear PhotoCORMs: Dioxygen-Assisted Carbon Monoxide Uncaging from Long-Wavelength-Absorbing Metal–Metal-Bonded Carbonyl Complexes. *Inorg. Chem.* **56**, 6094 (2017).

[2] T. Kurtikyan, A. Hovhannisyan, H. Minasyan, T. Mkhitaryan, A. Iretskii and P. C. Ford. Sulfoxide as a trans ligand to nitrogen oxide complexes of iron-porphyrins. ICBIC18 – International Conference on Biological Inorganic Chemistry. July, 31 – August, 5 – Brazil. *J. Biol. Inorg. Chem.*, **22**, S44 (2017).

[3] G. G. Martirosyan, A. A. Hovhannisyan, G. S. Hovhannisyan, A. V. Iretskii and T. S. Kurtikyan. Low-temperature spectral study of the novel six–coordinate dioxygen adducts of cobalt porphyrin bearing P- and S- trans donor ligands. V International Conference "Current problems of chemical physics. 25-29 September 2018, Yerevan, Armenia.

[4] G. G. Martirosyan, A. A. Hovhannisyan, G. S. Hovhannisyan, A. V. Iretskii, T. S. Kurtikyan. Weak coordination of H_2S to the solid-state ferrous porphyrin complexes with diatomic molecules. Characterization of 6-coordinate adducts at low temperature. *Inorg. Chim. Acta*, **482**, 894 (2018).

incorporated into this laboratory manual. Among other methods of reaction monitoring, the change in the solution conductivity and the change in gas pressure were implemented.

The result is a laboratory manual that consists of an introduction, 14 experiments, and an appendix:

1. Introduction.
2. Experiment 1. Phenolphthalein-NaOH kinetics.
3. Experiment 2. Reaction of magnesium with hydrochloric acid
4. Experiment 3. Reaction of Sodium Thiosulfate with Hydrochloric Acid.
5. Experiment 4. The Iodine Clock Reaction.
6. Experiment 4a. The Iodine Clock Reaction.
7. Experiment 5. Another Iodine Clock Reaction.
8. Experiment 6. Kinetics of the Oxidation of Ascorbic Acid by Hexacyanoferrate(III) ion. The Effect of Sodium Nitrate on the Reaction Rate.
9. Experiment 7. Aquation Kinetics of $[Co(NH_3)_5Cl]Cl_2$.
10. Experiment 8. Rate of Solvolysis of tert-Butyl Chloride.
11. Experiment 9. Acid Catalyzed Hydration of p-Methoxyphenylacetylene.
12. Experiment 10. Acidic Catalysis of Benzohydroxamic Acid.
13. Experiment 11. Base Catalyzed Deuterium Exchange Kinetics in Hypophosphite Ion.
14. Experiment 12. Kinetics of formation of the Cr(III)-EDTA complex.
15. Experiment 13 (Compare with Experiment 1). What Are the Kinetic Parameters of a Heterogeneous Reaction?
16. Appendix.
    a) Standardization of NaOH against Potassium Hydrogen Phthalate (KHP).
    b) Standardization of the H_2O_2 solution.
    c) Non-linear Curve fitting with Microsoft Excel Solver. Calculation of k_{obs}, k_{real} and Debye-Hückel plot.
    d) Report Organization.

Overall results of sabbatical leave.

1. I have established or strengthen close collaborations with University of California Santa Barbara (prof. P. C. Ford), Interkat Katalyzatoren, GmbH in Koenigswinter, Germany (Dr. J. Spengler) and The Scientific Technological Centre of Organic and Pharmaceutical Chemistry in Yerevan, Armenia (Prof. T. S. Kurtikyan).
2. A new laboratory manual for the CHEM363 course (Kinetics and Reaction Dynamics) was prepared and tested.
3. As a measurable result of my research work during the sabbatical leave 2 papers were published in peer reviewed journals with high impact factors and 2 presentations were given at international conferences.