

Oxidation of Halogenated and Polycyclic Aromatic Hydrocarbons using Rhenium-based Catalysts

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In this report, I am giving a summary of the research I did as a Fulbright scholar in 2002–2003 and also recalling the pleasant memories of a year spent in the United States. The original research project planned in my application had to be modified because rhenium-based compounds were not active as catalysts in the title reaction. However, less expensive iron complexes were active catalysts and helped me to discover that light has an important effect on the oxidation of chlorophenols in general. I developed a systematic way of comparing the efficiencies of different catalysts, worked with a new method for studying photochemical reactions, and began the long work of studying one particular catalyst in detail. The results were published in five different original research papers in the peer-reviewed chemical literature. In addition to my research, I also took part in the Fulbright Occasional Lecturer Program, created a website and gave a talk to commemorate the Kossuth bicentenary, and tried to make Hungary better known through a chemical presentation about the cyanide pollution wave that swept the Hungarian river Tisza in 2000.

1. Introduction

This is an unusual report in a number of respects. To begin with, the title was a major headache for me. I had to choose between two alternatives that seemed equally uncomfortable. The first choice was using the original project title of my application for Fulbright fellowship and not writing much about it in the report. The second choice was finding a title that reflects a little better on the research I actually carried out as a Fulbright scholar and at the same time confusing official records of my participation. After much agony, I decided to go for the first alternative and apologize for the grossly misleading title as a first thing in the introduction.

Why cannot I write about the research planned in my proposal? In fact, I can write about it four simple but honest words: it does not work. But the story is longer than that. I planned my application for a Fulbright scholarship in early 2001. The scholarship began in the summer of 2002. So I had to write a research proposal more than a year ahead. This is not easy in basic scientific research. When I was an undergraduate student, one of my professors told me something I still remember and believe: if you can predict the results of your research, you should not be doing it. Over the years, I have become convinced that good basic research is done to learn or discover something and not to confirm predictable phenomena. In my research proposal, I did my best to plan a particular research project in sufficient detail to be convincing even for specialists. However,

Mother Nature proved me wrong on one of my basic assumptions.

Another major problem with this report was the amount and depth of technical details I should include in it. As the scientific results of my work as a Fulbright scholar have already been published in the peer-reviewed chemical literature in five different original research papers¹⁻⁵, it seemed to be pointless to repeat them in a similar fashion. Neither it seemed to be wise for me to assume that the possible readers of this report would have the same level of chemical expertise the usual audience of my publications has. Finally, I have decided to put the emphasis on showing how exciting it was to work on this project and also write briefly about the non-scientific activities I was involved in as a Fulbrighter.

2. Research Project

As I have already mentioned, I could not do the research planned in my original proposal. The reason for this was that the rhenium compounds mentioned in the title did not have the expected effect on the studied chemical reactions. In this section, I will describe how I made this fact sure and what changes I made in the research strategy after this finding.

2.1. Scientific Background and Objectives

The organic compounds in the title, polycyclic aromatic hydrocarbons and halogenated aromatic compounds, are principal pollutants from incomplete combustions, and are of special environ-

mental concern due to their toxic, carcinogenic, potent mutagenic properties and ubiquitous presence in the environment. They are regarded as priority pollutants by both the United States Environmental Protection Agency and the European Union. These compounds are commonly found in the atmosphere both in the gas and particle phases. They are present in both surface and underground waters and were also shown to be resistant toward biodegradation.

The negative environmental impact of these compounds has been known for decades, and there have been considerable efforts in basic research to answer the challenge posed by them. Through the work planned in my original proposal I wanted to contribute to these efforts by combining my expertise in inorganic chemical mechanisms research and chemical kinetics with the use of rhenium-based catalysts under development in Prof. Espenson's laboratory in Ames, Iowa. A publication⁶ that appeared in *Science* magazine (one of the two leading scientific journals) in April 2002, shortly before the beginning of my grant period, convinced us to focus our research on chlorinated phenols. This subclass of compounds is produced by paper mills in the delignification of wood pulp by chlorine bleaching and is present in industrial sewage. Because of their toxicity, these compounds must be removed from sewage. A standard treatment method for organic pollutants is evaporation of water followed by incineration. For chlorinated phenols, this treatment method must be avoided as it produces sizeable quantities of extremely

toxic dioxins. Incidentally, one compound from the dioxin family received considerable attention from the international press in early 2005 when a story broke about its alleged use in an infamous 2004 assassination attempt against Ukrainian presidential candidate Viktor Yushchenko, who was later elected president.

An efficient method for the treatment of sewage containing chlorinated phenols would be to oxidize the chlorinated phenols completely, in other words, using an appropriate chemical to degrade these compounds to form water and carbon dioxide, which are harmless materials. The chemical used in this degradation process has to meet very stiff standards. It has to be cheap and widely available, more or less environmentally benign and should not form unwanted byproducts in considerable quantities. There are only three reactants that come close to meeting these tough standards: oxygen, hydrogen peroxide, and ozone. Ozone, in addition to its counterintuitive property of being highly toxic to humans, is not particularly cheap or widely available. Oxygen is notoriously difficult to use in reactions at ambient temperatures. In conclusion, hydrogen peroxide seemed the best choice. However, it is now well established that hydrogen peroxide reacts extremely slowly with chlorinated phenols and additional reactants are needed to accelerate the reaction in order to be useful for practical purposes. Such reactants are called catalysts in chemistry.

Prof. Espenson's research group has wide experience in using rhenium-based catalysts to facilitate chemical reactions

using hydrogen peroxide. This was a very nice coincidence for this project. We had compelling reasons to believe that these rhenium-based catalysts could be successfully used in the oxidation of chlorinated phenols. Although rhenium is a very rare metal and is expensive as such, the amounts needed for catalytic application are so tiny that this does not usually pose a major limitation on its uses, at least not in the chemical laboratory. In fact, the single most important industrial use of rhenium is also as a process catalyst.

2.2. Scientific Findings

The findings of my chemical research will be summarized in five subsections describing closely related results. I should mention that I usually worked on these experiments simultaneously and not independent of each other. As a consequence, the results and objectives of these seemingly different projects often mutually influenced one another in a way that is difficult to describe clearly.

2.2.1. Reasons for the Unsuitability of Rhenium-based Compounds to Serve as Catalysts

As my research project began in August 2002, I prepared one of the most generally applicable rhenium-based catalysts that has been successfully used to catalyze a vast number of reactions using hydrogen peroxide. This compound is called methyltrioxorhenium (abbreviation: MTO, chemical formula CH_3ReO_3). Within a week or so, I confirmed a complete failure

in attempts to catalyze the oxidations of different chlorinated phenols with MTO. In the experiments, the chlorinated phenol stayed intact without any sign of degradation, the only change observed was a slow and well known catalyst deactivation.

Later, I also had some chance to gain some insight as to why this reaction did not occur against the expectations. A chemical reaction does not usually consist of a single event in which all the reactant molecules are involved. It is much more common to have reactions with several simple steps one after another, each step involving the formation and break-up of only one or two chemical bonds. In a degradation reaction like the oxidation of chlorophenols, the number of bonds broken and formed is usually above 20 and may sometimes exceed even 50 implying that there must be quite a few simple steps.

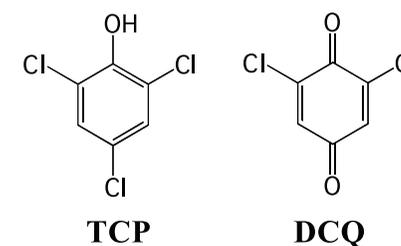
There are several different molecular ways for a compound to undergo oxidation depending mainly on the order of the bond-breaking and making processes. One of these ways is called 'oxygen transfer'. This means that the compound undergoing degradation accepts one or more oxygen atoms from various possible sources as the first step. For MTO, it is known that it works best when the first step in the degradation is oxygen transfer. However, it turned out that chlorophenols are not prone to oxidation by this oxygen transfer mechanism. Therefore, MTO is not a good choice for catalyst.

As this became clear, I went back to the chemical literature to search for

better catalyst candidates. There was no shortage of compounds with possible or proven catalytic activity.⁶⁻⁸ Many of these compounds contained some iron and I also noticed a structural motif that was common to an unusually high number of them. Finally, I decided to use several of them and compare their properties in a systematic way. But before that, I discovered something that was highly unexpected and is probably the single most important finding of the whole project thus far. In the next subsection, I will explain what this discovery was.

2.2.2. The Effect of Light on the Oxidation of Chlorinated Phenols

When I settled with a few promising iron-containing catalyst, I began mechanistic studies on their reactions. These mechanistic studies mainly involve experiments in which the time course of the target chemical reaction is studied. From the way the reactions evolve in time, it is often possible to draw solid conclusions on the order of the individual simple steps the overall process consists of. I used several different methods to follow the progress of the reaction. One of the most useful methods was a device called a chloride ion selective electrode. This is a simple piece of scientific equipment that can measure the amount of chloride ions present in a solution, no matter what other components there are in the mixture. The chlorine atoms in the structures of chlorophenols end up as chloride ions after the degradation reaction. So this electrode



gives a simple and selective way to follow the progress of the reaction. During the early studies, I used 2,4,6-trichlorophenol as a representative chlorinated phenol in the experiments. Its chemical structure is shown in Figure 1.

At first, the reaction times were quite long, often extending to a full day. Fortunately, the experimental equipment did not need constant human monitoring, so I could start an experiment at the end of the day, let it run through the night, and have a look at the recorded results next morning. Sometimes the experiments continued well into the next day as well. An important and in this case fortunate feature of the lab I worked in was that it was located somewhat below ground level and I had to have the lights on whenever I was in the room.

The first morning following an overnight experiment (October 16, 2002) I came to the lab but had something else to do for some time. Acting on a sudden impulse, I made a very unusual note in my research notebook: I recorded the exact time at which I came to the laboratory (8.10 am). Never before or after this day I did this again. After about an hour I arrived, I began processing the data from the experiment that was still running. To my great initial surprise, the data showed that the rate of

chloride ion formation suddenly increased at some point in time. This was extremely unusual. The rate of almost any chemical reaction decreases as time passes. Even in the rare cases where such acceleration is observed, it is a gradual process and not a sudden change. My sudden acceleration was small, but significant. It definitely called for an explanation.

The rate of a chemical reaction may depend on a number of outside factors. However, outside factors are usually controlled and kept unchanged during a single experiment. A sudden change like the one I saw could only be due to an outside effect that changed within a very short time period. At this point, I made a crucial calculation which determined the exact time when the sudden acceleration began. This would again be highly unusual in normal research because the rate of chemical reactions only depends on the time that elapses after starting the reaction. However, the sudden acceleration was anything but normal. It turned out that the sudden acceleration occurred at 8.10am, exactly at the time I arrived. It was clear that I somehow did something that changed the rate of the reaction. My best hypothesis was that turning the light on caused the effect. There was a very convenient way to prove this explanation. The experiment was still on, I just had to illuminate the sample deliberately with an intense light source and see whether this influences the rate or not. I found a powerful lamp in the laboratory almost immediately and did the experiment with spectacular results: the rate increased enormously. The chloride ion concentrations

measured in this single highly conclusive experiment are shown in Figure 2.¹

In a subsequent flurry of research, I made sure that light has an effect on the degradation reactions of all chlorophenols – no matter what the catalyst or the oxidizing agent is. This was an important finding for two very fundamental reasons. First, this effect was previously unreported in the literature. Scientist doing earlier related research took no precautions to avoid the effect of light, therefore their conclusions had to be critically revised. Second, it could be advantageous to improve the cost-efficiency of an industrial sewage treatment process simply by exposing the treated sewage to sunlight.

On a more personal note, I have to admit that I was lucky to find this light effect so early on. Several fortunate circumstances helped me in this finding but I hope that this whole story also falls into a category for which there is an age-old scientific saying: 'chance favors the prepared mind'. I am sure I would have made this discovery without the fortunate coincidences because my usual experimental procedures are careful enough to reveal hints of light effects even if I am not looking for them intentionally. However, without this luck, the discovery could have taken a lot longer and could have rendered a huge body of experimental work inconclusive.

2.2.3. Detailed Studies on Light-driven Chemical Reactions – a Case Study with Simultaneous Improvement of Experimental Methods

When the light effect became clear there were two evident lines of research to follow. The reaction was accelerated by light, but it also proceeded without illumination. So one possible way to continue was to do further experiments in the dark. This was in agreement with the scientific methods used from the dawn of systematic research – a good experimenter identifies and separates the important outside factors and handles them one at a time. The other direction was to find the actual reaction the light brings about by photochemical investigations, learn about it as much as possible and try to improve its efficiency. I decided to pursue both of these possible lines.

Even if there were no practical way to improve the efficiency of the actual industrial water treatment methods by illumination, it would have been less than satisfactory intellectually not to find a reason for the light effect. At first, finding a logical explanation posed quite a bit of a challenge. The huge problem was the first law of photochemistry. This law states that only light absorbed by some of the reactants may have any effect on a chemical process. Although chlorophenols, hydrogen peroxide, and the catalysts used all have absorption in the ultraviolet light range, the degradation reaction was also

accelerated by visible light, which none of the reactants absorbed. Finally, the experiments revealed that a compound named a chlorinated quinone is formed in an early reaction step of the degradation and consumed in a later one. Quinones usually absorb visible light (consequently they are colored) and so do chlorinated quinones. What is more, quinones are known to undergo photochemical reactions and these reactions have been studied in considerable detail because of scientific interest unrelated to the degradation of chlorinated phenols. So the light absorption and subsequent photochemical reactions of chlorinated quinones explain why even visible light influences the rate of the reaction.

I took this opportunity to work on an idea that had been brewing in me for some time by then. This idea was basically to develop a new experimental technique for studying photochemical reactions. Usually, photochemical studies require specialized instrumentation. This equipment is readily available in many laboratories throughout the world, but simpler methods would also be welcome. The idea was that a commercially available and much more common piece of instrumentation called diode array spectrophotometer has a pair of powerful lamps which are intense enough to force photochemical changes. Thus, this instrument can drive the reaction and detect the changes at the same time. Although the instrument is not designed to carry out photochemical investigations, we showed that it can still provide valuable information on light-related

processes. The initial study was done on the photochemical reactions of a selected chlorinated quinone named 2,6-dichloro-1,4-benzoquinone. Its chemical structure is shown in Figure 1. Using this method, it was possible to clarify mechanistic points in this photoreaction.²

2.2.4. Comparison of different iron-based catalysts

Despite my efforts to identify and study the processes responsible for the light effect, the main interest in the reactions remained elucidating the mechanisms of the reactions taking place without illumination. As I already mentioned, there were a number of earlier studies published in the literature. These studies typically focused on characterizing the properties of one particular catalyst in detail, often using specialized and expensive instrumental techniques to draw conclusions. I was surprised to find that no efforts to compare the different catalysts systematically had been reported in the literature in spite of the relatively large number of individual systems studied.⁶⁻⁸ So I decided to work on a protocol that uses relatively simple instrumentation and makes quick comparison possible.

My systematic study defined and measured three different stoichiometric and two kinetic efficiencies for the catalysts in the oxidation of 2,4,6-trichlorophenol by hydrogen peroxide. Six different iron-based activators were used to make the comparison: $\text{Fe}^{3+}(\text{aq})$ (from a simple iron alum), $\text{Fe}(\text{TPPS})^+$ (a water soluble iron-containing porphyrin that is similar to the iron-containing compounds in human blood),

$\text{cis}-[(\text{cyclam})\text{Fe}]^{3+}$, $\text{trans}-[(\text{cyclam})\text{Fe}]^{3+}$, $[\text{Fe}(\text{TPA})]^{2+}$, and $[\text{Fe}(6\text{-Me}_2\text{-TPA})]^{2+}$ (these four are synthetic compounds that have been used successfully to catalyze similar reactions). The systematic chemical names for the abbreviated ligands are: TPPS = meso-tetra(4-sulfonatophenyl)porphine, cyclam = 1,4,8,11-tetraazacyclotetradecane, TPA = tris(2-pyridylmethyl)amine, 6-Me₂-TPA = bis[(6-methyl-2-pyridyl)methyl](2-pyridylmethyl)amine. These ligands and their iron(III) complexes were usually not available from chemical suppliers and had to be prepared individually. The stoichiometric efficiencies of the catalyst were characterized by comparing the total organic carbon content, chloride ion concentration, and remaining oxidant concentration to the ideal stoichiometry where carbon dioxide, water and inorganic chloride are the only products. The kinetic efficiencies of the catalysts were compared using the rate of chloride ion formation and H_2O_2 consumption. The final conclusion was that $\text{Fe}(\text{TPPS})^+$ is probably the best catalyst overall and all five other catalysts have advantages and drawbacks.⁵

2.2.5. Detailed studies with one catalyst

Once I identified the complex $\text{Fe}(\text{TPPS})^+$ as a promising catalyst, it was clear that this compound is worth having a closer look at. So I carried out detailed studies to explore the mechanism of the catalytic reaction. This basically means finding out the sequence of simple steps involving only a few bond-breaking and making events through which the reactions proceeds. The usual way to do this

is to study the time course of the reactions using a number of different initial concentrations for each reactants. For a reaction that is as complicated as the total degradation of 2,4,6-trichlorophenol, this usually assumes years, if not decades, of experimental work, some of which is routine but also often requiring creativity. During the last part of my Fulbright scholarship, I dedicated my experimental efforts to beginning this long process of research.

It became clear that 2,4,6-trichlorophenol is first transformed to 2,6-dichloro-1,4-benzoquinone and other chlorophenols react in a manner that shows full structural equivalence. I studied the kinetics of these reactions in detail, clarified the exact role the catalyst plays during the reaction and also showed that the initial and catalytically highly active form of the catalyst is transformed to a much less active form as part of this first process. So it is clear that the catalyst could be further improved by a structural modification which makes this deactivation process a lot slower.³ With different chlorophenols I also studied structure-reactivity relationships for this particular step. The finding was quite surprising: the reaction did not show the usual structure-reactivity relationship patterns but there was an unexpected close correlation between the rates of the reactions and a structural indicator of the different molecules that can be measured by nuclear magnetic resonance at carbon-13 isotopes. Further research should make clear what this close correlation exactly implies and show whether similar correlations hold for other types of reactions as well.⁴

I also began studying how this first important intermediate compound, 2,6-dichloro-1,4-benzoquinone further reacts in the course of the overall reaction. The finding was that this compound can react with hydrogen peroxide without a catalyst being present. In this process, an oxygen atom is added to this compound to form 3,5-dichloro-2-hydroxy-1,4-benzoquinone. Although a catalyst is not needed in this process, the presence of $\text{Fe}(\text{TPPS})^+$ significantly alters both the rate and the product of the reaction. The product of the catalytic oxidation could not be identified positively, but it seems to be likely that the six-membered carbon-ring of 2,6-dichloro-1,4-benzoquinone opens up during the process.⁴

2.3. Significance and Dissemination of Findings

The results of the research done during my one-year Fulbright scholarship have been published in the peer-reviewed chemical literature in five separate papers.¹⁻⁵ The spectacular effect of light on the oxidation of chlorophenols seemed to be a rather significant new finding which merited rapid publication in a non-specialized chemical journal. We chose the journal *Chemical Communications*.¹ The results of the photochemical studies were published in a widely read photochemical journal named *Journal of Photochemistry and Photobiology A: Chemistry*.² It took an unusually long time to publish the results comparing the efficiencies of different catalysts, but finally this paper came out in the journal *Green Chemistry*.⁵ The editor of this journal decided to award the special title

'Hot Article' to this paper, indicating that the results reported in it are of unusually high scientific quality and importance.⁹ The results of the detailed studies of the Fe(TPPS)⁺-catalyzed reactions were published in two parts: the first in *International Journal of Chemical Kinetics*³ and the second in *New Journal of Chemistry*.⁴ All of these five journals are peer-reviewed meaning that two or three scientists, who are experts in this field, check the experimental design, the data processing, the presentation and the conclusions of the paper and the work is only published if they think it meets the generally accepted scientific quality standards.

2.4. Continuing the Research

When I finished my Fulbright scholarship in the summer of 2005, I was convinced that I had to continue this kind of research after returning to Hungary. I managed to do so in collaboration with Prof. István Fábrián, a full professor of inorganic chemistry at my home institute. The American host institution also helped me to start as they allowed me to ship most of the important specialty chemicals needed for this research to my home University in Debrecen. At the first occasion possible (in May 2004) I also applied for separate research funding to the Hungarian Research Fund OTKA. In January 2005, I was informed that my application was successful and I can continue this special line of research for four years with a budget of about HUF 1,000,000 (\$ 5000) per year. Prof. James H. Espenson, who

was a very generous host of my Fulbright scholarship, is about to retire in the summer of 2005 and this will bring our highly successful collaboration to an end. I still hope to maintain contact and share research projects with researchers at Iowa State University, especially with Dr. Andreja Bakac and Prof. William Jenks. After part of the research was published, I also began collaboration with Terrence J. Collins at Carnegie Mellon University in Pittsburgh, PA. His group is very active in developing high-performance catalysts, one of which he already sent me for detailed study.

Since the end of my Fulbright scholarship in 2003, I have continued working with the water soluble catalyst Fe(TPPS)⁺. The new method developed for studying photochemical reactions seems to prove its usefulness beyond my most optimistic expectations. In the cerium(III)-catalyzed autoxidation of sulfur(IV), this method gave spectacular and significant new results.¹⁰ One graduate student changed her research project to use this method for studying the autoxidation of sulfur(IV) with other catalysts. She has completed an impressive series of creative experiments and is expected to defend her PhD in late 2005.

3. Beyond Research – a Fulbrighter on Mission

3.1. A Chemist's Way of Talking about Hungary in the USA

One of the major objectives of the Fulbright Program is trying to promote mutual understanding between scholar's home countries and the United States of America. Grantees are very much encouraged to make individual efforts to serve this goal of the program. One of the ways to do this is to try to make Hungary and Hungarian culture known in the United States and vice versa. At first, I could not see clearly how I could contribute to this significantly with my scientific experience. Then I began to understand that my work done in connection with the infamous cyanide spill in the Hungarian river Tisza that occurred in the year of 2000 probably provides the best opportunity for me to advance such goals. At that time, my home university was heavily involved in related research. One particular possible cyanide treatment method using ferrous sulfate received a lot of popular attention after a story on the News of Hungarian TV2 reported that the massive fish kills could have been avoided using this method. At the Department of Inorganic and Analytical Chemistry of the University of Debrecen I was part of a group studying the possible application of this method. Our final conclusion was negative: the risks of using this method were clearly

unacceptable and the idea itself, although it was without doubt creative, was based on incomplete information about the chemical composition of the cyanide-containing waste that spilled into the river. However, this negative conclusion was based on experiments and ways of thought that could have been interesting for chemists in general. So I decided to prepare a 50-minute presentation about the cyanide spill and the possible remediation methods. Within this presentation, I had ample opportunity not only to discuss the related chemistry, but also to speak about the geography and history of Hungary.

In June 2002, I managed to obtain the footage from the News Program of Hungarian TV2 that ran the story. (I owe an acknowledgement to Mr. György Bernáth, the news director of the channel.) I prepared two different versions of the presentation: one suitable for inorganic chemists with a lot of specific information, and another suitable for the general public requiring no special knowledge in chemistry. I gave this presentation four times during my tenure as a Fulbright Scholar, twice at my home institute in Ames, Iowa, once in Los Angeles and once in Las Cruces, New Mexico. Two of this occasions were for inorganic chemist audiences, the other two were for the general public.

3.2. Kossuth Bicentenary

Before leaving Hungary for the US in the summer of 2002, I noticed that 200th anniversary of the birth of Hungarian statesman Lajos Kossuth would be during my visit on September 19, 2002. I was determined to make this fact known at Iowa State University. This attempt was especially fitting because Iowa has a county named after Lajos Kossuth in the northern part of the state. Previously, even Historians not familiar with this fact would have guessed that the word Kossuth found on Iowa maps had some sort of Native American origin similarly to a number of other county names in Iowa.

In late August, I started a small website about Lajos Kossuth, the bicentenary, and the connection to Iowa. I was very happy when Mr. Joseph M. Isenberg, an Iowa State historian contacted me and asked me to talk about Lajos Kossuth at one of the meetings of the local Phi Alpha Theta Association. The meeting was held exactly on September 19 and was a very nice occasion to pay tribute to one of the greatest Hungarian politicians of all times. I was also very happy to find out that the library of Iowa State University holds a copy of a rare book about Lajos Kossuth which was published in America in 1851. I checked this book out and presented it during my talk.

At the meeting it turned out that my host, Mr. Isenberg had been an American Fulbrighter in Romania the previous year. At the end of the event, he gave me a book titled 'A History of the American People' by Paul Johnson. I enjoyed reading most

of this book and learned a lot about the history of the United States of America. However, it was great disappointment for me to find that the description of the last few decades was heavily biased toward one of the significant political forces in American life and sometimes sounded like a fundamentally partisan judgment on certain politicians rather than a scholarly and objective description of historical events I was expecting.

3.3. The Fulbright Occasional Lecturer Program

Fulbright scholars in the United States can take part in the Fulbright Occasional Lecturer Program, which fund trips to visit academic institutions within the United States other than the host institution of the grantee. I had the good luck of being invited to the University of California at Los Angeles by one of its inorganic chemistry professors, Prof. Mahdi Abu-Omar. Following the usual schedule of such visits, I talked to faculty members, students, and gave a presentation in the afternoon. The timing of this trip (February 2003) was chosen so that I could also participate in a conference held close to Los Angeles, the Gordon Research Conference on inorganic reaction mechanisms. I am still in frequent contact with Prof. Abu-Omar, who moved to Purdue University in Indiana in the meantime.

My second and last trip as a Fulbright Occasional Lecturer was to a minority serving institution, New Mexico State University, on the invitation of Prof. Michael D. Johnson. I had a schedule similar to the one at UCLA, but I gave

two separate presentations, one about the cyanide pollution wave and another about my research in inorganic reaction mechanisms. The visit became especially memorable as I also had an opportunity to meet Prof. Ralph Wilkins, who is one of the leading authorities within the field of inorganic reaction mechanisms. I had not met him in person before this visit, but I had known his classic textbook quite well.

3.4. Other Activities

In addition to the visits as a Fulbright Occasional Lecturer, I was also invited to present my earlier research at the University of Minnesota at Minneapolis by Prof. Lawrence Que Jr. I was more than happy to drive the three hours from Ames to Minneapolis and had a very good time there.

In the summer of 2002, I joined the American Chemical Society (ACS), which is the largest professional society in the world with its membership close to 160000. One of the most important activities of the Ames local section was to organize ACS-sponsored professional lectures. These were very interesting and useful lectures, hopefully also including the one where I was the invited speaker. Another memorable ACS lecture was presented by Prof. Ronald De Lorenzo, who had decades of experience in writing popular essays about chemistry. I thought this collection of short essays was rather impressive and could be very useful in Hungary as well. I decided to translate them into Hungarian and publish them on the World Wide Web. I contacted the author and obtained his permission for

this project. Although I could not spend as much time translating as I originally planned, 101 translated essays are already published on the website of the Chemistry Department at the University of Debrecen.¹¹ I think membership in ACS is a very significant asset in my professional career primarily because of invaluable access to the articles in chemical journals published by ACS. After returning to Hungary, I took part in establishing a Hungarian Chapter of ACS and still serve as the webmaster of its website.

An invaluable part of the time spent in the United States was the exposure to an international research community that cannot be found anywhere else in the world. Only within the research group I joined, I worked together with specialists from China, Jordan, Canada, India, Japan, Russia, Croatia, Iran, and Ethiopia. I also enrolled into the new faculty training program of Iowa State and got a taste of what being a professor at an American research university involves.

Finally, among the many people I met in Ames, I was very glad to make friends with Prof. Richard Cruse from the Department of Agronomy of Iowa State University, who has regular contact with Hungarian researchers and still works together with a Hungarian graduate student.

4. Summary

I feel that the Fulbright scholarship in 2002-2003 is a defining moment in my career. I started my own independent research with great success, I began international collaborations and was invited to a number of universities other than my host institute. After an eventful year as a Fulbright scholar, I returned to Hungary determined to continue my research and my work as a university faculty member and at the same time staying in close contact with those who helped me so much in the United States.

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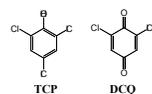


Figure 1. Chemical formulas of 2,4,6-trichlorophenol (TCP) and 2,6-dichloro-1,4-benzoquinone (DCQ)

Figure 2. Effect of light on the formation of Cl^- during the oxidation of 2,4,6-trichlorophenol (TCP) by hydrogen peroxide catalyzed by $\text{Fe}(\text{TPPS})^-$. $[\text{TCP}]_0 = 0.83 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 50 \text{ mM}$, $[\text{Fe}(\text{TPPS})^-]_0 = 5.0 \text{ }\mu\text{M}$, $T = 25.0 \text{ }^\circ\text{C}$, $\mu = 0.1 \text{ M (NaNO}_3\text{)}$; F = fluorescent room light turned on; L = halogen lamp turned on. Inset: part of the curve between 770 and 1000 min showing the accelerating effect of room light.

