MEMORIES OF MICHAEL POLANYI IN MANCHESTER

Melvin Calvin

[***EDITOR'S NOTE:*** *The following article is a transcript of an address by Professor Melvin Calvin (Department of Chemistry, University of CA, Berkeley) given at the Berkeley Polanyi centennial conference on March 15, 1991. Professor Calvin, who did postdoctoral study with Polanyi in Manchester more than fifty years ago, became a Nobel Laureate in 1961 for his studies of the sequence of chemical reactions in photosysthesis*]

It was in the course of writing my thesis at the Univerity of Minnesota that I first became familiar with the work of Professor Michael Polanyi, who was then at the University of Manchester in England. Manchester therefore with Polanyi in the Chemistry Department, seemed like a very interesting place to work, and the research that Polanyi was doing there, (on the nature of chemical reactions and the theory of transition states in chemical reactions) seemed to be the type of research I wanted to join in. I wrote to Polanyi in the hope that he could help me obtain postdoctoral support to work in his laboratory. He was able to do this, fortunately, through the auspices of a grant he had from the Rockefeller Foundation. So, at the end of my thesis work in Minneapolis, I undertook to spend a period of time with Professor Polanyi in Manchester. This postdoctoral period began in the fall of 1935, and was the most fortunate thing for my entire research career that followed.

When I first met Michael Polanyi in Manchester in 1935, he was well into second career. You know he had at least three careers at least that I know about, maybe four. Originally he had been a physician and moved to Berlin and served in the Hungarian Army. He then took up Chemistry. He reached Great Britain in flight from Germany in the early thirties. He had begun some particularly sophisticated studies in Berlin that he was to conclude at Manchester within a relatively short time. He then began still another career, that of a political scientist-economist- philosopher. I saw the beginning of that in Manchester. Toward the end of my stay there, in 1937, it got so it became difficult often for me to talk with him because he was thinking in terms of economics and philosophy, and I couldn't understand his language.

There is no doubt in my mind that the experience I had with Polanyi was instrumental in opening my eyes to the advantages of an interdisciplinary approach to science. He had the type of mind that was curious about all things, even those not involved in his current work. I feel that my experience with Michael had a profound effect on my subsequent career.

I kept in close touch with Polanyi over the years until his death in 1976 at the age of 85. The last time I saw him personally was when I was George Eastman Professor at Oxford in 1967. He was there then, having moved from Manchester. I didn't get very close to him at Oxford, but I did see him. Our relation in Manchester was very personal, but in Oxford it was more distant. You know I was used to him in Manchester as very personal, but in Oxford it didn't happen that way.

I can remember very vividly rambling conversations in Manchester that took place in Polanyi's office toward the end of my first year, in 1935. I had been working exclusively on platinum-hydrogen activation systems. Let me tell you what that means. Chemists understand, but others do not. Hydrogen is a gas, very unreactive by itself. But when it comes in contact with platinum, it breaks up into two atoms that migrate around on the platinum surface, and are very reactive, with almost anything they touch. That is what we were investigating.

Polanyi pointed out that most biological oxidations and reductions were mediated by a porphyrin molecule such as a heme, that is the red color of blood cells and the green of chlorophyll, which is present in most of the biological oxidation and reduction catalysts or chlorophyll, the photo catalyst in plants. Both the red of blood and the green of plants have the same skeleton structure; they are different otherwise. If biological oxidation was a dehydrogenation and reduction, that is, a hydrogenation reaction which took place on porphyrin, then it should be possible to do a study on porphyrin molecules similar to the study we had been doing on platinum using molecular hydrogen as one of the reagents. Now I would be using porphyrin crystals instead of platinum. Of course the natural biological oxidation-reductions that have porphyrin as the active groups take place on proteins, and Polanyi speculated that the proteins were simply wires for moving electrons around to match the protons that had ultimately to be removed. He gave me the idea; I don't know whether he believed it or not. The important reactions therefore took place on porphyrin molecules themselves. At least to my mind this was a remarkable feat of association on Polanyi's part. Thus it became important for me to find porphyrin molecules that might be useful in studying hydrogen activation. Hydrogen is a very inert gas. It needs to be activated and it reacts to all kinds of things, but you have to get it started. The way most chemist start it is by having the hydrogen molecule which is two atoms tucked together, sit on platinum and they come apart, and then each hydrogen atom works separately.

We had to find a porphyrin redox catalyst model stable enough to be used in a gas experiment at a variety of elevated temperatures. Now you couldn't use the ordinary porphyrin like chlorophyll or heme. They were unstable at temperatures we have to use. So I had to make some that would be stable for my purpose. The ordinary naturally occurring porphyrin that could be obtained from hemoglobin, catalase, or any of the other porphyrin-containing biological catalysts were not stable enough for this purpose. However, about this time, Polanyi heard of the synthesis of a porphyrin analog in London by R. P. Linstead, one of the leading organic chemists of Great Britain. Linstead's discovery of the phthalocyanines (really tetraazaporphyrins) occurred as a result of an accident in the ICI Factory that was manufacturing phthalonitrile). Apparently one of the glass-lined kettles that was used to make phthalonitrile from phthalamide cracked, and the whole reaction mixture turned a deep blue color. This happened as a result of contact of the reactions mixture with the iron of the kettle. Linstead, instead of throwing it away, successfully undertook the project of finding out what the source of the color was. If you are a good scientist, that's what you do. Polanyi, a highly imaginative thinker, recognized that phthalocyanines were structurally very similar to chlorophyll and to heme, and were very much more stable as well. In fact, they were some of the most stable dyestuffs known. He thought he could use this synthetic compound with its high stability as a model of chlorophyll and heme. In that way we might learn something about the fundamental nature of that particular structure, one so important in biology for its catalytic functions.

I was sent by Polanyi down to Linstead's laboratory in Imperial College in London to learn how to make and purify phthalocyanine. That is when I became an organist chemist. I spent a few relatively easy days in the laboratory because the synthesis of phthalocyanine was a very simple procedure. After a few experimental trials and errors, it was found that the metal of choice for the center of the phthalocyanine ring of four nitrogens was zinc.

Having succeeded in preparing both metal-free and metal-containing phthalocyanines, we undertook a study of the activation of molecular hydrogen in the gas phase by crystal of these materials. This was one of my first forays into synthetic organic chemistry, and it so happened that I was becoming acquainted with a class of compounds that were to be of major importance throughout my scientific life. I am still working on them, and they are so many and so varied that I don't get tired of them.

The studies on phthalocyanine dyes led to my interest in another coordination compound, chlorophyll, and eventually to the study of photosynthesis for which I am best known. The impulse to study photosynthesis also arose from another aspect of coordination chemistry that I was involved with in World War II. There was a concatenation of two different lines of work. We were trying to devise methods for recovering uranium and plutonium from nuclear reactor materials. We developed a synthesis for coordination compounds that we had designed, and those compounds proved to be successful; that is, they would pull the uranium and plutonium out. This scientific continuity actually extends to our work even today in the area of artificial photosynthesis. It all stems from my interest in coordination chemistry which began at the University of Manchester with Polanyi. How many years ago that? Over fifty! I am still working with the same kind of stuff at a much more rarified level.

During these post doctoral years in Manchester (1935 to 1937), I became aware of the freedom of thought that allowed me to undertake work in any area of science that seemed appropriate to the questions I was faced with. That was Polanyi's habit of mind. Nothing stopped him. He would do whatever had to be done, and I got that virus from him. It's not a bad one, you know. One of the basic tenants of our scientific work in photosynthesis has always been to go in whatever direction the light may lead. In this case, perhaps, the original flashlight was the coordination chemistry and phthalocyanine.

Before I finish, I would like to say a few words about the other students with whom I shared Polanyi's interests. Both were graduate students working on hydrogen activation problems in the adjacent laboratory. One of them, E.C. Cockbain, worked for many years at the Malaysian Rubber Research Institute in London. More recently, starting in the middle eighties, our paths crossed again as members of the scientific advisory board of a new biotechnology company here in the United States. The other student, Dan Eley, became a professor of physical chemistry at Nottingham. I met him in Nottingham in 1958 when I received a honorary degree there, and also in 1986 when I presented the Holden Botany Lectures at Nottingham. There is no doubt that Michael Polanyi had a profound effect on the careers of all three of us and many others as well.

I considered my time spent at Manchester with Michael Polanyi as scientifically exciting and crucial in the development of my own personal philosophy of using an interdisciplinary approach to the solution of any scientific problem.