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AT THE ACADEMIC/INDUSTRY INTERFACE

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In recent years it has become very fashionable to rediscover and applaud one somewhat vague phenomenon of our modern technical society known as "the academic/industry interface". There is truly a renaissance of interest in this phenomenon and entire meetings, studies and even organizations are being devoted to its praise and promotion. But, looking beyond the slogans and platitudes, what is really meant by "the academic/industry interface" and what is really substantive and important about it? Some who have chosen to search for significance have not found it in the window-dressing programs but have found it in those interactions sometimes described as one-on-one programs. These are interactions between an academic scientist and an industrial scientist who share a strong real and common interest in some area of research and who have established a truly effective give and take relationship in a complimentary search for knowledge and for useful profitable results. I should like to share with you a few recollections of and reflections on one-on-one interactions that I and several other former colleagues at Monsanto had with Jack Halpern that led to some extremely important results both in science and technology during the past two decades.

In 1964, fresh from the successful development at Monsanto of a heterogeneous catalyst that was commercialized for making linear olefins for biodegradable detergents, I was given a vote of confidence: an opportunity to expand into new areas of catalysis. While it was somewhat out of phase with the trends at that time, we elected to launch a substantial new program at Monsanto in homogeneous catalysis. In clear imitation of the work being conducted in most other industrial laboratories, we chose to pursue the then-hot area of oxy-metallation reactions with particular emphasis on palladium catalysts. Our program was young, our thoughts were naive and we became cautiously adventurous. Instead of studying oxy-metallation reactions of lower olefins such as ethylene and propylene, we explored the much less studied area of higher olefins. The results were interesting and immersed us in the fascinating world of homogeneous catalysis, but we sensed the need to do much more if we were to establish a world class effort. We needed to expand our program by hiring new staff members who were educated in relevant fields such as inorganic and organometallic chemistry. We needed to establish appropriate laboratory facilities and, most of all, we needed to seek and obtain expert guidance. For this guidance, we turned to one of the world's leading academic scientists in homogeneous catalysis: Jack Halpern.

First, we made arrangements with Jack to provide us in May 1965 directly at our Research Center with an intensive one week course in Homogeneous Catalysis. The

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course met and exceeded all of our hopes and expectations. It was during that course that I first learned about the general nature of oxidative additive reactions and specifically about the facile oxidative addition of methyl iodide to metal complexes. This knowledge was to prove eventually to be of crucial value. Later in 1965 we consummated a consulting agreement with Jack broadly in the field of homogeneous catalysis and then started to recruit and hire some of his students, the first of whom was his postdoctoral student, Dr. Frank Paulik.

When Frank arrived, we were open to suggestions for his initial research. Building upon the knowledge and experience he acquired in Halpern's laboratory, Frank suggested exploring the chemistry of rhodium and iridium complexes. After he observed reversible complexation of certain arylphosphine complexes of rhodium both with olefins and carbon monoxide, we speculated that these complexes might be useful as catalysts for the hydroformylation of olefins to aldehydes. Indeed, they were! And we launched a substantial effort in rhodium hydroformylation catalysis that paralleled and supplemented research in this area in several other industrial and academic laboratories in the world. We observed that, in contrast to the cobalt carbonyl complexes then in commercial use, the rhodium-based catalysts in the presence of excess phosphine ligand provided better overall properties in terms of product linearity, catalyst stability and high activity at relatively low reaction pressures. At that particular time, we had in progress in Monsanto a series of weekly conferences that were widely attended by scientists and research managers from all segments of the company. Upon hearing about the low pressure hydroformylation properties of the rhodium phosphine complexes, Dr. Walter Knox, research director of the Petrochemicals Division, aware of an impending drastic cost reduction in the price of methanol, asked whether our hydroformylation catalyst might achieve low pressure carbonylation of methanol to acetic acid. This question prompted and triggered our studies of methanol carbonylation.

A couple of experiments aimed at methanol carbonylation were attempted with the rhodium hydroformylation catalysts, but the results were totally negative. We speculated that the problem might reside in the difficulty of forming a metal–carbon bond with methanol which could not coordinate with rhodium via the pathway accessible to olefins of metal-hydride insertion. Recalling the lectures of Jack Halpern on oxidative addition and the facile addition of methyl iodide to metal complexes, we then decided to add an iodide promoter and, in the very first experiment with added iodide, observed the catalytic carbonylation of methanol to acetic acid. It was a total of 11 days between the first unsuccessful experiment and the successful one using added iodide. While the concept of promoting metal–carbon bond formation via oxidative addition of methyl iodide was valid, the actual rhodium complexes involved in the catalysis appear to be drastically different from the arylphosphine complexes that were first charged into the reaction medium.

It was only a total of five months from the very first experiment aimed at finding a low pressure carbonylation catalyst to the transfer of the project from Corporate Research to the operating division with the assignment of 30 people to the development of a commercial process. Several people contributed significantly to this feat: Dr. Arnold Hershman who elucidated the remarkable kinetics of the reaction (zero order in both reactants (methanol and carbon monoxide) and whose work (some still unpublished) first led to the conclusion that oxidative addition of methyl iodide was the rate-determining step; Dr. John Craddock who was Frank Paulik's supervisor and who contributed significantly to the planning and organization of the catalyst development effort; and Dr. Denis Forster who first identified the true structure of reactive intermediates and also elucidated the nature and chemistry of side reactions. Jack Halpern served as an extremely valuable consultant throughout in the exciting discussions of reaction kinetics and mechanistic pathways.

The Monsanto acetic acid process is an extraordinarily successful technology. It has been cited as one of the outstanding achievements in industrial catalysis in the decade of the 1970's and stands as the most notable example of C_1 chemistry substituting for an earlier hydrocarbon process (the ethylene-based Wacker process for acetic acid). Underpinning these accomplishments were invaluable contributions derived directly or indirectly from the interaction with Jack Halpern. These included (1) the training of Frank Paulik which led us to initiate research on rhodium complexes without which we may not have moved into hydroformylation with rhodium catalysts; (2) his own basic research on oxidative addition reactions which led us to the key discovery of the iodide promoter; (3) his educational prowess which imparted knowledge to several of us previously unschooled in homogeneous catalysis and (4) his stimulating consultations which always promoted a striving for understanding and excellence.

There were many fields and areas of encounter with Jack Halpern over the years, but I would like to recall and reflect very briefly on only one other: the arena of asymmetric hydrogenation catalysis. The pioneering work of Dr. W.S. Knowles of Monsanto in this area is well-known and, through its application to the production of L-Dopa, led to the world's first major commercialization of asymmetric synthesis using a totally synthetic catalyst. Jack Halpern and Bill Knowles discussed Knowles' work many times and, in particular, the origin of the asymmetric catalysis. Eventually Bill supplied some optically active materials to Jack and Jack initiated in his own laboratories a program of fundamental research on the kinetics and mechanism of asymmetric hydrogenation of prochiral molecules. The work of Halpern in this field stands among the most elegant and distinguished research in the annals of homogeneous catalysis. The results contradict the lock-and-key concept of the origin of stereoselectivity and may have implications regarding the behaviour of enzymic catalysts. I would like to believe that the interactions with Knowles facilitated, if not stimulated, the fundamental research by Halpern in this area.

In my 33 years of industrial research, I have encountered no better example of the academic/industry interface than that which I and others were privileged to share with Jack Halpern. He and his work stand as eminent examples of how basic academic research can and does nurture industrial innovation.