Journal of Inclusion Phenomena and Molecular Recognition in Chemistry 7 (1989), 3–6.

Iwao Tabushi (1933–1987)

My only close association with Iwao Tabushi being limited to a period of about two weeks in Kyoto when I, together with my wife, visited Kyoto on his invitation, I cannot lay claim to a long standing personal intimacy with him. Nor for that matter can I claim to be expert over the wide range of chemical behavior which he explored in his research so diligently and productively. Still, even in the short time that I interacted with him, this altogether remarkable man impressed me so strongly by his qualities as a human being, and by the way that he addressed his professional interests that I feel moved to add my own testimony to that made by others in commemorating him.

As I look back on our altogether too brief an association, the impression left with me that comes through most strongly is his generosity. He gave generously of his time and his energies, from what seemed an inexhaustible reserve of vitality, in sharing professional interests, and in seeing even to the details of accommodation

and travel arrangements for what appeared to be a steady stream of visitors to his laboratories. This generosity extended also to social arrangements which invariably included the accompanying individuals and involved on occasion his colleagues, usually some or all of his coworkers, sometimes his wife, Sakiko, and almost always himself. I continue to marvel at his tact and restraint, when even at a late evening hour his enjoyment of the occasion never seemed to flag, knowing as I did that after parting with the last lingering guest, he would return to his laboratory to the work that he enjoyed so keenly.

So great was his enjoyment of his work and his enthusiasm for new ideas and new results that it is altogether likely that the late hours in the laboratory in the company of some of his coworkers were refreshing. At any rate, when I would see him the next day, even after we had spent a long evening together, there was no diminution in his clarity of thought, nor of his enthusiasm as our discussions turned to his research interests. This is not to say that he lacked interest in the work of his visitors – they were given ample opportunity to present their results and views in public seminars. Besides, though I was aware of Tabushi's reputation prior to my visit to Kyoto, I was well informed only about a small part of his work, and it was clearly in my interest to acquaint myself with a wider range of his activities.

As much as anyone I have known Tabushi was the complete chemist. His involvement in research was not limited by the traditional subject boundaries: both his interests and capabilities transcended them. Nor was he limited by a concern with whether his research was basic or applied; he tried to understand Nature and equally he tried to put his knowledge to use. His training was that of a physical organic chemist, and he had a firm grasp of the physico-chemical principles that underlie that discipline. At the same time, he had an imposing command of descriptive chemistry, organic and inorganic. His multifacetted approach to chemistry is illustrated, though inadequately, by the following excerpts taken from rather recent papers selected from the approximately 200 he published.

"A comprehensive model of the inclusion process of α-cyclodextrin is presented herein. Van der Waals interaction energy, Allinger's conformation energy, solvation energy of apolar solute in water, hydrogen bond energy of water molecules in the cavity of α-cyclodextrin hexahydrate, and all other possible energies were taken into account for the calculation of free-energy change by complexing an apolar guest molecule by α-cyclodextrin. Motional freedoms of all the particles relevant to the inclusion phenomenon were taken into consideration." ('Approach to the Aspects of Driving Force of Inclusion by α-Cyclodextrin', I. Tabushi, Y. Kiyosuke, T. Sugimoto and K. Yamamura, *J. Am. Chem. Soc.* (1978), **100**, 916.)

"Picket-fence porphyrin (TpivPP)-iron-*N*-methylimidazole-O_2 complex is used as an artificial P-450, and the decomposition rates are investigated in details in the presence of HCl and H_2-colloidal platinum supported on poly(vinylpyrrolidone) with or without addition of benzoic anhydride. From the decay rates of the oxy complex followed by electronic spectrum under a variety of conditions, pseudo-first-order rate (with the complex) constants are obtained." ('Kinetics and Mechanism of Reductive Dioxygen Activation Catalyzed by P-450 Model System. Iron Picket

Fence as a Catalytic Center', I. Tabushi, M. Kodera, and M. Yokoyama, *J. Am. Chem. Soc.* (1985), **107**, 4466.)

"Concept of coupling between oxidation and generation of pH gradient across membrane is presented by use of artificial liposome modified with electron transport catalysts, cyt c_3 or C_4V^{++}. The presented coupling mechanism based on facilitated 'down-hill' electron flow, electroneutrality preservation and permeability control is confirmed by independent and direct measurements." ('Basic Principle of Coupling between Oxidation and pH Gradient Generation. Artificial Liposome Digesting H_2', I. Tabushi and T. Nishiya, Tetrahedron Letters, (1982), **23**, 2661.)

"Molecular design of uranyl specific ligands is reviewed. Basic principles to characterise the unique nature of uranyl complexes are scrutinized from ligand field calculations, crystallographic analyses and stability constants of various complexes. The most typical characteristic of uranyl coordination is a planar hexacoordination by anionic ligands giving rise to the formation of the 'ate-complex.' Several macrocycles were synthesized by the appropriate combination of these principles. Approaches to recovery of uranium from sea water are briefly reviewed. Organic chelating resins are the most promising candidates for the practical adsorbent". ('Molecular Design of Specific Uranophiles', I. Tabushi and Y. Kobuke, *Israel J. Chem.*, (1985), **25**, 217.)

The excerpts also serve to indicate what the major themes in Tabushi's research were toward the end of his career. His work on cyclodextrins was begun in 1976. The motivation was to gain an understanding of molecular recognition processes and, armed with such understanding, to mimic – in this particular instance – hydrolytic enzymatic processes. Even his early work in modifying cyclodextrins so as to increase catalytic activity and selectivity attracted world-wide attention, and his position as a pioneer in this active and important field of research is secure.

Tabushi's interest in biomimetic processes extended also to oxidation-reduction enzymes. His success in this field can be gauged from these quotations taken from an article published in *Japan Chemical Week* (April 17, 1986) under the heading 'Efficient Proc. for Oxygen Activation Pioneered'.

"A research group led by Professor I. Tabushi of Kyoto University has successfully developed a new process to activate oxygen using an artificial system modeled on cytochrome P450 enzyme. This process is more than 1000 and $5 \sim 6$ times more efficient than conventional methods and natural enzyme, respectively . . .

"Their study is 'ultimately' aimed at pioneering artificial livers. The liver biochemically decomposes poisonous substances and synthesizes biomaterials. Cytochrome P450 is involved in such biochemical processes.

"The said study has paved the way for realizing an artificial system which resembles a natural enzymatic reaction process and which is needed for conditioning the existence of biomaterials. It is expected to be applied to the industrial-use oxidation process in which benzene and paraffin are transformed into phenol and alcohol, respectively."

It should not be thought that Tabushi's interest in the biological processes was restricted to invention. Invention grew out of understanding, and understanding grew out of research, at the most basic level. An important such interest was the study of electron transport and attendant ion transport through artificial membranes, where again pioneering and definitive experiments were performed in his laboratories. I make specific mention of this interest because it provided the greatest overlap between his research activities and my own, and this overlap accounts for his sponsorship of my visit to his laboratories.

On an earlier occasion I wrote this about Tabushi:

"Few match his passionate devotion to research and his intensity of effort. He is an inspiring leader of a large group that contains a high proportion of gifted individuals. Their quality accounts in part for the productivity of the laboratory. It is however mainly to be credited to Professor Tabushi himself. He is very imaginative and ingenious. He is quick to master a new subject area, and to find in it opportunities which others have missed. Ideas are soon translated into action in his laboratories, and his entire research group is driven by Tabushi's restless energy, where he sets an example by his own remarkable diligence."

I mourn the loss of a gifted scientist, and the early termination of what promised to be for me a warm and rewarding friendship.

H. TAUBE