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Obituary

Prof. Kenichi Fukui 1918–1998

Theoretical chemist who created the fundamental theory of chemical reactivity*

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Dr. Kenichi Fukui, professor emeritus of Kyoto University and Director of the Institute for Fundamental Chemistry died of cancer on 9 January 1998. He was awarded a Nobel prize in 1981 jointly with Prof. Roald Hoffmann for their theories of chemical reactivity. In recent years, as Director of the Institute for Fundamental Chemistry founded in Kyoto in 1988 to honor his Nobel Prize, Professor Fukui continued to play a leading role in the field of fundamental chemistry in Japan. At the same time, as the country's first chemistry laureate, he was very busily occupied with official obligations as well as public appearances. Despite all these burdens, he remained active in science until his death.

Professor Fukui was born on 4 October 1918, in a rural district of Nara prefecture not far from Kyoto and Osaka. Nara was the ancient capital of Japan in the eighth century. Here at the fountainhead of Japanese culture and tradition, Professor Fukui spent his childhood in surroundings that are full of history and beautiful nature. At that time, he was interested in history and literature, and his daily life was often spent walking and running around the hills and fields, sometimes collecting insects. Later, he remarked that if he had any genuine gift, it had been brought about by the close interaction with nature during his childhood.

In 1931, he entered the Imamiya Middle School in Osaka, and after finishing 4 years of study instead of the normal 5 years, he passed the entrance examination of Osaka High School. After completion of 3 years of high school, he was admitted to the Department of Industrial Chemistry, Faculty of Engineering, Kyoto Imperial University in 1938.

In his middle and high school days, he excelled in mathematics and physics, but showed little interest in chemistry. At that time, chemistry was regarded as a field of empirical science. The reason why he selected industrial chemistry upon entering university was explained by himself explicitly as follows [1]. "In my high school years, chemistry was not my favorite subject. The most decisive event in my educational career, however, occurred when my father asked for the advice of Prof. Gen-itsu Kita of Kyoto Imperial University, a native of the same district and senior of him, concerning the major his son should choose. Professor Kita suggested that he should send his son to the Department of Industrial Chemistry where Professor Kita was teaching." Professor Kita's advice was extremely biased: "If he likes mathematics, let him do chemistry."

Professor Kita graduated from the Department of Applied Chemistry, Faculty of Engineering, Tokyo Imperial University in 1906. After studies in Tokyo, he moved to Kyoto as Professor of Kyoto Imperial University in 1921. Although he was not an expert in quantum mechanics (which was discovered in 1926), he understood by intuition that chemistry was likely to be vastly influenced by this new physics in the future. This might be the reason why he suggested Professor Fukui major in chemistry. In this sense, it can be said that Professor Kita sowed the seed of the first Nobel prize in chemistry in Japan. Professor Kita showed his splendid talent not only in scientific research but also in management of the Department. He renovated the old curriculum by introducing lectures on pure chemistry by professors of the Department of Chemistry, Faculty of Science. Furthermore, following the suggestion by Prof. Shinjiro Kodama, a former student and a colleague, he established a chair of theoretical physics at the Department of Industrial Chemistry in 1943. Thus, Prof. Gentaro Araki, a theoretical physicist, started to give lectures on chemical physics and mathematics, and Yonezawa and Nagata, the present authors, were among the first students attending his lectures. This was the first theoretical physics chair and the first lecture on quantum mechanics in any chemistry department in an engineering faculty in Japan.

*Contribution to the Kenichi Fukui Memorial Issue

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After his graduation from Kyoto Imperial University in 1941, Professor Fukui was engaged for a few years in experimental research on synthetic fuel chemistry in the Army fuel Laboratory. The results brought him a prize in 1944. He was appointed a Lecturer of Kyoto Imperial University in 1943, became Associate Professor in 1945 and was promoted to Professor in 1951. As an associate professor, he worked with Professor Kodama on the design of the catalytic reaction plant and was in charge of the theoretical analysis and design. Professor Kodama, a student and a successor of Professor Kita and a teacher of Professor Fukui, followed the same innovative line and established a new unique institution, the Department of Fuel Chemistry, which was later reorganized into the Department of Hydrocarbon Chemistry. Professor Fukui had been affiliated to this department throughout his academic life at Kyoto University.

Professor Kodama stressed the importance of cooperation in chemistry between theoreticians and experimentalists, and he encouraged Professor Fukui to promote his theoretical research. "To achieve great things, being a great man is not enough: you also need to be in the right place at the right time" [2]. Although Professor Fukui was a greatly talented scientist, he was lucky to have a chance to be involved in theoretical research at this department under the warm encouragement of Prof. Kita and Kodama. In addition, the time was also favorable. An exciting atmosphere prevailed over the field of chemistry as the newly established quantum mechanics seemed to offer insights into all fields of chemistry including organic reactions.

In early spring of 1951, a fire broke out at this department and forced Professor Fukui and his staff to use the same room as Professor Haruo Shingu, an organic chemist dealing with hydrocarbon chemistry. Heated discussions were made between Professors Fukui and Shingu on chemical reactions of organic compounds. A well-known and enigmatic problem in organic reactions was the reaction site in naphthalene; namely, electrophilic substitution such as nitration occurs predominantly at the α-position. This fact, however, could never be explained by organic electronic theory, because it had been proved theoretically by the Coulson–Rushbrooke theorem that the total π-electron densities on all carbon atoms of naphthalene were equal to unity. One day, an idea flashed in Professor Fukui's brain that not all the π-electrons, but the electrons in a particular orbital might play a dominant role in organic chemical reactions. This idea came from the analogy with the outer valence electrons in atoms, so he assumed the special role of electrons in the highest occupied molecular orbital (HOMO). Immediately he calculated the electron distribution in the HOMO using the Hückel method, and found that the electron density at the α-position was definitely larger than that at the β-position. This episode shows clearly that the birth of the frontier electron theory was the product of a discussion between a theoretical chemist and an experimental organic chemist. In this sense, it resembles the collaboration between Woodward and Hoffman which resulted in their rules.

Encouraged by the first success for naphthalene, the electron distributions in the HOMO for 15 unsubstituted aromatic hydrocarbons were calculated by a hand-driven mechanical calculator and compared with the actual positions of electrophilic attack. Agreement between the position of largest electron density and the experimental position of electrophilic attack was perfect without exception, and this result was published in 1952 [3]. Subsequently, nucleophilic substitution was found to be correlated with the position of the largest electron density in the lowest unoccupied molecular orbital (LUMO), and in the reaction with radicals, both the HOMO and the LUMO were found to be involved [4]. The HOMO and the LUMO were designated as frontier orbitals and the electrons in these orbitals as frontier electrons.

When Professor Fukui proposed the frontier electron theory in 1952, there were only two staff members, Drs. Yonezawa and Nagata, and no student in the theoretical section of Fukui's laboratory. Dr. Yonezawa extended the theory to the fields of reactions of saturated compounds, addition reactions of conjugated compounds, and polymerization reactions of vinyl compounds. Dr. Nagata applied the theory to biological phenomena, especially cancer production by chemical compounds. Polycyclic aromatic hydrocarbons such as benzo[a]pyrene (3,4-benzpyrene) were known to be potent carcinogens, but their carcinogenic mechanism was totally unknown at that time. An intimate correlation was found between the frontier electron density at specified positions of aromatic hydrocarbons and their carcinogenic activities, and the result was published in 1955 [5].

In 1964, Professor noticed an important role of the symmetry of frontier orbitals when dealing with the Diels–Alder reaction [6]. Thus, the symmetries of the HOMO and the LUMO of dienes and those of the LUMO and the HOMO of dienophiles, respectively, were found to be important for the concerted cyclic interaction between them. In principle, this idea is the same as that of the Woodward–Hoffmann rule [7], although the latter was more elaborate and has wider applicability. In fact, Professor Fukui stated in his Nobel lecture as follows [1]. "It is only after the remarkable appearance of the brilliant work by Woodward and Hoffmann that I have become fully aware that not only the density distribution but also the nodal property of the particular orbitals have significance in such a wide variety of chemical reactions." On the other hand, Professor Hoffmann [8] wrote that "the Woodward–Hoffmann rule was a primitive frontier orbital approach, developed intuitively and graphically, and buttressed by simple molecular orbital calculations. Our idea of a controlling orbital was in the spirit of Fukui. And indeed Fukui could right away derive all of our conclusions." Furthermore, he stated that "For Kenichi Fukui and me, science for once worked the way it should on the human level – instead of a competition there developed a friendship". We are deeply impressed by the fact that two prominent scientists respected each other and improved their theories through their friendly cooperation.

Professor Fukui was a scientist who devoted all his efforts throughout his academic life to clarifying the principle of chemical reactions. Of his 280 papers in English, about 200 are concerned with the theory of chemical reactions and related subjects. His passion to elucidate the principle of chemical reactivity did not fade until his death. At the same time, he was deeply concerned about environmental problems and the protection of the earth from the pollution caused by human activities. He insisted that protection of the earth from pollution is a primary duty for chemists, and he believed that it is achievable by the concerted efforts of chemists and through the wisdom of human beings.

References

1. Fukui K (1981) Nobel lecture: The role of frontier orbitals in chemical reactivities. The Nobel Foundation, p 147
2. Moses V (1997) Nature (Lond) 385: 586
3. Fukui K, Yonezawa T, Shingu H (1952) J Chem Phys 20: 722
4. Fukui K, Yonezawa T, Nagata C, Shingu H (1954) J Chem Phys 22: 1433
5. Nagata C, Fukui K, Yonezawa T, Tagashira Y (1955) Cancer Res 15: 233
6. Fukui K (1964) In: Löwdin PO, Pullman B (eds) Molecular orbitals in chemistry, physics and biology. Academic Press, New York, p 513
7. Woodward RB, Hoffmann R (1965) J Am Chem Soc 87: 395
8. Hoffmann R (1998) Nature (Lond) 391: 750