



Letter

Enthusiasm and philosophy of Professor Juro Horiuti

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Abstract

This is a reminiscent story of a great scientist. Through the research on homogeneous acid–base catalysis achieved on the basis of his philosophy, how he emphasized the importance of logic, exact expression, deep thinking, and hard work is retrospected.

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1. Introduction

It is my real pleasure and deep emotion to reminisce Prof. Horiuti in commemoration of his centennial birthday. I worked as a student and a staff member in the Research Institute for Catalysis (RIC), Hokkaido Univ. under his direction for 15 years from 1950, the year I entered his laboratory, to 1965, the year he retired. During the period, I did the research on homogenous acid–base catalysis which he ordered me to do. When I started the research, I was only one researcher engaged in homogeneous catalysis among 24 staff members in RIC and so felt lonely. Since I was in such a special situation, Prof. Horiuti always encouraged me, saying that homogenous catalysis and enzyme catalysis are important for understanding heterogeneous catalysis. He used to say the principle of catalysis is the same in any cases.

The elucidation of the decomposition mechanism of chloroform in aqueous solution was my research subject, which he gave me by the reason that even the reaction mechanism of the simplest organic molecule, CHCl_3 , was not exactly understood at that time. We

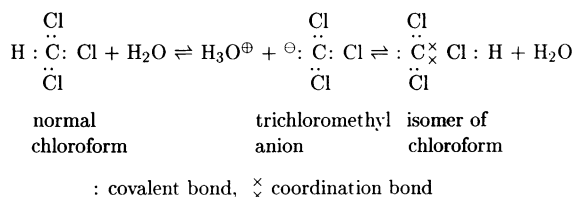
measured the rate of the decomposition of CHCl_3 to CO and HCl, the rate of hydrogen exchange between CHCl_3 and D_2O , and the rate of chlorine exchange between CHCl_3 and Cl^- , using radiochlorine $^{36}\text{Cl}^-$, in the range of $\text{pH} = 0\text{--}14$ and in the absence of oxygen. It took 5 years to complete the experiments with high accuracy, which needed several newly developed techniques. Prof. Horiuti himself joined the chlorine exchange experiment for 1 year, since the experiment using radiochlorine was the first time in Japan and any techniques were not known.

Analyzing those kinetic data by a rate theory developed by Prof. Horiuti, we proposed a mechanism of chloroform decomposition consisting of four elementary steps where carbon dichloride (a carbene) and isomer of chloroform were included as intermediates [1–5]. At almost the same time, Prof. J. Hine in Georgia Institute of Technology proposed a different mechanism by a method of physical organic chemistry, which included carbon dichloride as an intermediate, but not isomer of chloroform [6,7].

Anyway, Prof. Hine's and our papers both of which suggest the existence of carbon dichloride contributed to the progress of carbene chemistry which was becoming one of the focus of the world's attention.

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Although I was satisfied with the unexpected contribution, Prof. Horiuti had been never satisfied with it. His interest was to make clear the difference between Hine's mechanism and our mechanism, in other words, whether isomer of chloroform exists or not. Our experimental fact that a maximum rate appeared at pH = 4 in the pH dependence profile of the rate of chloroform decomposition supports our mechanism, but not Hine's mechanism. Thus, Hine and Lungford followed our experiment, but could not observe the rate maximum, indicating that our mechanism is not valid [8]. However, they used buffer solutions of ionic strength = 0.2 to determine the rates at different pH, since otherwise pH shifts due to HCl formed during the reaction, while, in our case of ionic strength = 10^{-3} – 10^{-5} , the rates were determined from time change of pH ($d[H^+]/dt$). Therefore, the key point for the appearance of the rate maximum was thought to be due to the difference in ionic strength. Then, Prof. Horiuti ordered us to exactly measure the rates at different ionic strengths. We confirmed first that the rate maximum appeared at low ionic strengths and then observed that the rate maximum decreased with increasing ionic strength and finally disappeared [9,10]. The observed effect of ionic strength was well interpreted only by assuming a remarkable effect of ionic strength (salt effect) on activated complex of the elementary step of the formation of chloroform isomer from trichloromethyl anion and proton.



The rate-determining step of chloroform decomposition was concluded to be the elementary step of the formation of chloroform isomer below pH = 4 and the elementary step of the formation of carbon dichloride by simultaneous attack of both acid and base to isomer of chloroform above pH = 4. It was surprising and intriguing to me that an isomer of chloroform was predicted by the kinetic analysis and that the salt effect on an activated complex was outstanding. I remember Prof. Horiuti used to say these kinds of fundamental researches undoubtedly contribute to a definite progress

in science, though it may take 50 years until the value is recognized. This was his philosophy. I extended his research method to the other compounds such as CCl_4 , CH_2Cl_2 , $\text{C}_6\text{H}_5\text{CHCl}_2$, $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$, and $\text{C}_6\text{H}_5\text{CCl}_3$ to elucidate their decomposition mechanisms in aqueous solution.

Almost a half century has passed since that time. It is a pity, however, that not much attention has not been paid to the isomer of chloroform, the pronounced salt effect, and Prof. Horiuti's original rate theory of homogeneous acid–base catalysis. Extreme originality seems too difficult to understand in some cases. It is certain, however, that his characteristic research method and philosophy exerted important influences on my later research on heterogeneous catalysis by solid acids, solid bases, and solids having acid–base pair sites. I sincerely thank him in heaven for his great direction.

Through the research on chloroform, I had many opportunities to discuss various problems with Prof. Horiuti. His characteristics I strongly felt are as follows:

- (1) Thorough logic which led to exact expression.
- (2) Strong concentration power which led to deep thinking.
- (3) Extraordinary hard work.

2. Logic and exact expression

There are a few stories concerning how Prof. Horiuti attached importance to strict logic and exact expression. In a seminar which was held once a week in RIC, a researcher introduced the content of a scientific paper. Prof. Horiuti asked him many questions, but was not satisfied with his answers which were not logical and/or not exactly expressed judging from Prof. Horiuti's standard and so even for a simple question the discussion continued for 5–10 min, the time spent for the seminar being several hours. The speaker was so tired and exhausted that he could not say anything and finally fell down on the floor. Then, someone poured a bucketfull water on him. As soon as he recovered, the seminar started again. At the end of the seminar, Prof. Horiuti said to him, "Finish kindergarten as soon as possible". In the other case, he said to a speaker, "You lack a quality of science". All of the

staff members including professors, lecturers, and research assistants had more or less similar experiences.

One day, Prof. Horiuti asked me to answer a question, “Describe a thumbtack without drawing the picture”. I could not concisely and exactly answer the question. I needed many sentences to describe it (in Japanese). He said I should make more efforts on logical thinking and exact expression. According to him, English was compulsory subject even for science and technology course students in Massachusetts Institute of Technology (MIT). The students complained against it, because their native language is English and English is not so necessary for science and technology. In the first lecture of English, a professor set the examination concerning the description of thumbtack mentioned above. The result of the examination was that the answer papers of all students became red by the correction with red pencil. After that, the students did not complain any more and recognized the importance of logic and exact expression. When we submitted our papers to scientific journals, Prof. Horiuti corrected the manuscripts I wrote in English usually seven to eight times and even those written in Japanese five to seven times. Not much difference in the correction times between English and Japanese was also due to the problems in logic and exact expression.

3. Concentration power

Prof. Horiuti’s concentration power was surprising, which led to his deep thinking. He always emphasized that thinking is more important than learning or studying. He said to us, “Don’t read literatures or papers of scientific journals, because wide knowledge disturbs thinking”. I asked him, “If we don’t read literatures, the research we are doing may have been published already by others. It is dangerous”. He answered, “We need not worry about it, since our work achieved by deep thinking is absolutely original”.

There is a proverb.

A person who learns widely but doesn’t think deeply is dark.

A person who thinks deeply but doesn’t learn widely is dangerous.

Prof. Horiuti who belonged to the latter category emphasized that a person who attained a high level of

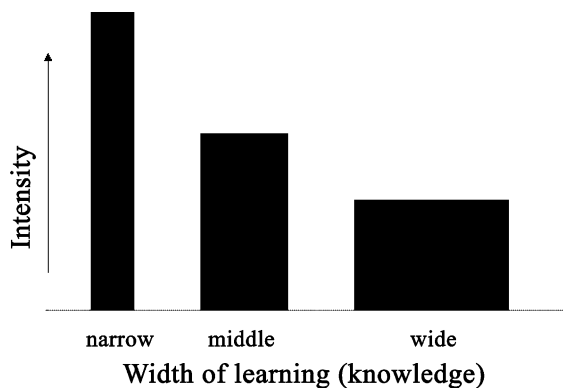


Fig. 1. Intensity of deep thinking vs. width of learning.

the intensity of deep thinking has a high possibility of achieving original and creative work. Fig. 1 which he used to draw shows a relation between the intensity of deep thinking and the width of learning in the case that the total capacity of the intensity and the width is the same. The person of the high intensity can see new things (new theory, new phenomena, etc.) which the persons of the lower intensity are difficult to see. The latter persons having wider already-known knowledge are difficult to create new things and may be suitable for simple teachers who teach only knowledge and don’t give any impacts.

Prof. Horiuti was enthusiastic also in education in the sense mentioned above. Although the weight ratio of research to education was generally 2:1 or 3:1 in Japanese universities a half century ago, he insisted the ideal ratio should be 1:1. He gave us a lecture of physical chemistry in which quantum mechanics and statistical mechanics occupied about 50%. However, in the examination which was oral, the questions he asked were “What is rate constant?”, “What is a pure substance?”, etc. Many students could not exactly answer and had to have re-examination. He put stress on fundamental understanding which is more important than simple learning.

4. Hard work

His hard work was extraordinary. I recall the old days in 1950–1955 when I did the research on chloroform. It is no exaggeration to say that the number of days Prof. Horiuti worked was 364 per year during

the above period. The only 1 day he did not work was 2 January, when he invited all staff members of RIC to his home for a new year dinner. Everyday he entered RIC at 7 o'clock and usually left there at 22 o'clock. When he left RIC at 19 o'clock, he worked at his home for 3 h from 3 to 6 o'clock in early morning. Thus, his working time in both cases was 15 h per day and his sleeping time was 5–6 h. He spent most of his time for analyzing experimental data and writing papers with deep thinking which produced new research plans and for discussion with the staff members. Since everyday including Sunday and holiday he asked each staff member, "What is new experimental result", we (in particular, unmarried staffs) could not have Sundays and holidays except 1 week summer vacation. His hard work caused our complete devotion to our research experiments.

5. Conclusion

Sixteen years ago when I visited Prof. Olah, he gave me a chance to listen to Prof. Barton's lecture entitled "How to get Nobel Prize". Prof. Barton mentioned modestly that important factors for the title were as follows:

- (1) A chain of logic.
- (2) Intuition.
- (3) Hard work.

Although Prof. Horiuti hated intuition because it is not science, he may have agreed with the importance

of intuition in the case that intuition originates from logic and deep thinking. Intuition which is also important for discovery and creative work generates also from keen observation and insight into phenomena and also from revelation which comes from a relation between a knowledge and another knowledge. In the present days of excessive informations, how to get effective informations (knowledge) is a problem.

Anyway, Prof. Horiuti gave us a definite direction that logic, concentration, and hard work are important for developing science. I remember a Greek philosopher's word. What is greatness? "Greatness is to give a direction to people. In other words, to show which way people should take." In this sense, Prof. Horiuti was great.

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