

## LABORATORY OF HIGH PRESSURE CHEMISTRY

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This laboratory started in 1957 as a new section separated from Kodama Laboratory (Head: Prof. Dr. Shinjiro Kodama). The laboratory has been investigating high pressure organic synthetic chemistry, and on the other hand, though does not appear in the title, kinetical and mechanistic research on the free radical and atom reactions in gas phase as a main theme, too.

### 1. High Pressure Chemistry

As to the high pressure chemistry, effort has been devoted mainly to the gas and liquid (solid) reactions, to synthesize useful products such as aromatic aldehydes, carbonic mono- or dibasic saturated or unsaturated acids *etc.*, using carbon monoxide, carbon dioxide or hydrogen under the pressure of some hundred atmospheres as a reactant, and as substrates aromatic hydrocarbons, olifins, halo-benzenes, phenols, styrene, cyclohexene, alcohols allylic compounds, or aqueous alkali and even the solid material such as alkali acetate are used and the catalyst used are HF-BF<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, alkali carbonates, and PdCl<sub>2</sub> (and its complex).

The character of researches is mainly fundamental, *i.e.*, the reaction rate (and equilibrium) is being analyzed to establish the reaction mechanism, the results of which will be seen in the publication list at the end of this section.

### 2. Free Radical Chemistry

In this part, investigation on the rate constant determination and on the detailed mechanism of the elementary reactions involving free radicals and atoms in gas phase which are produced by various methods *e.g.*, (vacuum) ultraviolet photolysis, microwave discharge and combination of radicals and/or atoms produced by the above-mentioned processes for the production of unsaturated radicals. The technics utilized here are, a dynamical Time-of-Flight mass spectrometry and spectrometrical measurement for transients and the usual G-C analysis for stable products.

The character of the research is also kinetical, and the detailed mechanism of the unimolecular decomposition or isomerisation of chemically activated species such as methyl allyl ether, pentyl, 1-butene-1 or -4 yl radical has been elucidated with the aid of RRKM theory, further, on some reactions of O, Cl, NO<sub>2</sub>, NO, N researches are now going on.

On the other hand, computational simulation of the process of photochemical air pollution utilizing the known rate data of some 100 elementary reactions is now in progress.

## Publications

(\* indicates an article published in Japanese)

### I High Pressure Chemistry

1. Y. Takezaki, T. Teraoka, N. Sugita, H. Teranishi, and K. Kudo: The Reaction of m-Xylene with Carbon Monoxide under Pressure, *Kogyo Kagaku Zasshi (Journal of the Chemical Society of Japan)*, **69**, 907 (1966).\*
2. K. Kudo and Y. Takezaki: Synthesis of Alkali Molonates from Alkali Acetates, Carbonates, and Carbon Dioxide under High Pressure, *ibid.*, **70**, 2147 (1967).\*
3. Y. Takezaki, A. Inoue, N. Sugita, H. Teranishi, and K. Kudo: Reaction of Anisole with Carbon Monoxide under Pressure, *Bull. Japan Petroleum Inst.*, **9**, 45 (1967).
4. K. Kudo, N. Sugita, H. Teranishi, and Y. Takezaki: Reaction of Phenol with Carbon Monoxide under High Pressure in the Medium of Hydrogen Fluoride and Boron Fluoride, *J. Japan Petroleum Inst.*, **11**, 16 (1968).
5. Y. Takezaki, H. Teranishi, N. Sugita, and K. Kudo: High Pressure Syntheses of Aromatic Aldehydes (Review), *Rev. Phys. Chem. Japan*, **38**, 69 (1968).
6. M. Kanbara, N. Sugita, K. Kudo, and H. Teranishi: Kinetic Study of the Addition Reaction of Carbon Monoxide with Ethyl Fluoride in Hydrogen Fluoride under High Pressure, *Bull. Japan Petroleum Inst.*, **11**, 48 (1969).
7. N. Sugita, T. Yasutomi, and Y. Takezaki: High Pressure Synthesis of Succinic Acid from Acrylic Acid and Carbon Monoxide, *ibid.*, **12**, 66 (1970).
8. K. Kudo, N. Sugita, and Y. Takezaki: Kinetic Study of Potassium Molonate Synthesis from Potassium Acetate, Carbonate, and Carbon Monoxide under Pressure, *Nippon Kagaku Kaishi*, 1082 (1973).
9. H. Yoshida, S. Sugita, K. Kudo, and Y. Takezaki: Kinetics on Palladium Catalyzed Carbonylation of Allyl Chloride under Carbon Monoxide Pressure, *ibid.*, 1002 (1974).
10. H. Yoshida, N. Sugita, K. Kudo, and Y. Takezaki: Kinetics on Palladium Carbonylation of Iodobenzene under Carbon Monoxide Pressure, *ibid.*, 1386 (1974).
11. N. Sugita, T. Furuta, K. Kudo, and Y. Takezaki: Kinetic Study of Addition of Carbon Monoxide to Methallyl Chloride in Hydrogen Fluoride under High Pressure, *ibid.*, 1379 (1974).
12. A. Yanagase, N. Sugita, K. Kudo, and Y. Takezaki: Kinetic Study on the Synthesis of Methyl Glycolate from Methylene Sulfate and Carbon Monoxide under Pressure, *ibid.*, 583 (1975).
13. H. Yoshida, N. Sugita, K. Kudo, and Y. Takezaki: Kinetics on the Formylation of Iodobenzene Catalyzed by Palladium (II) Chloride in a Pyridine Solution, *Bull. Chem. Soc. Japan*, **49**, 1681 (1976).
14. H. Yoshida, N. Sugita, K. Kudo, and Y. Takezaki: Kinetics on the Carbonylation of Cyclohexene in a Methanol Solution Catalyzed by Palladium (II) chloride-Triphenylphosphine, *ibid.*, **49**, 2245 (1976).
15. J. Osugi, Y. Takezaki, and A. Makita: Evaluation of P-V-A relations—The Most Probable Values of Compressibility Factor of Methane, *Rev. Phys. Chem. Japan*, **41**, 61 (1972).

### II Free Radical Reactions

1. Y. Takezaki and S. Mori: Determination of Micro-Reactor Volume from the Transient Concentration Profile by Means of a Time-of-Flight Mass Spectrometer and the Application to the Rate Constant Measurement of Fast Reaction,  $O + NO_2 \rightarrow NO + O_2$  and  $N + NO \rightarrow N_2O$ , *Bull. Inst. Chem. Res., Kyoto Univ.*, **45**, 388 (1967).
2. A. Ibuki and Y. Takezaki: Primary Processes in the Flash Photolysis of Dimethyl Carbonate Vapor, *ibid.*, **45**, 406 (1967).
3. A. Ibuki and Y. Takezaki: Primary Processes in the Flash photolysis of Dimethyl Carbonate Vapor II—Discrimination of the Hydrogen Producing Primary Processes, *ibid.*, **47**, 240 (1969).
4. Y. Takezaki and S. Mori: Investigation of Chemical Dynamics by Means of TOF Mass Spectrometer (Review), "SO-Hanno-Sokudoron". "Kagaku" special issue No. 38 p. 187 (1969).
5. M. Takeuchi and Y. Takezaki: Chemical Reaction of Hydrocarbons in the Microwave Discharge— I. On the Mechanism of the Decomposition of Ethane and Ethylene, *Bull. Inst. Chem. Res., Kyoto*

- Univ.*, **49**, 230 (1971).
6. M. Kawasaki, T. Ibuki, M. Iwasaki, and Y. Takezaki: Vacuum-Ultraviolet Photolysis of Ethylene Oxide, *J. Chem. Phys.*, **59**, 2076 (1973).
  7. M. Kawasaki, M. Iwasaki, T. Ibuki, and Y. Takezaki: Primary Processes of the Photolysis of Ethyleneimine at Xe and Kr Resonance Lines, *ibid.*, **59**, 6321 (1973).
  8. A. Ibuki, T. Murata, and Y. Takezaki: Isomerization of Chemically Activated Propenyl Radicals: *J. Phys. Chem.*, **78**, 2543 (1974).
  9. A. Ibuki and Y. Takezaki: The Reaction of Hydrogen Atoms with Acetylene, *Bull. Chem. Soc. Japan*, **48**, 769 (1975).
  10. T. Ibuki, A. Tsuji, and Y. Takezaki: Isomerization of Chemically Activated 1-Buten-1-yl and 1-Buten-4-yl radicals, *J. Phys. Chem.*, **80**, 8 (1976).
  11. T. Ibuki and Y. Takezaki: Unimolecular Decomposition of Chemically Activated Methyl Allyl Ether, to be published in *Int. J. Chem. Kinetics*.