

KODAMA LABORATORY (July 1943~July 1957)

Head: Dr. Shinjiro Kodama

and

TAKEZAKI LABORATORY (June 1957~)

Head: Dr. Yoshimasa Takezaki

Takezaki laboratory started in 1957 as a new section separated from Kodama Laboratory (Head: Prof. Dr. Shinjiro Kodama), and on the retirement of Prof. Kodama (1957) some of his research themes were succeeded by this laboratory.

Prof. Kodama, who succeeded the Prof. Dr. Kita's Laboratory in 1943 when the fundamental research and the industrial development on Fischer-Tropsch gasoline synthesis had been proceeding, accomplished this work, and during the War he began the investigation on polyethylene synthesis and along with the physico-chemical studies he developed high pressure techniques (more than 1,000 atm.) and operated a pilot plant, which was the first foundation of polyethylene industry of to-day's prosperity in Japan.

Takezaki Laboratory is the one organized to apply high pressure techniques thus developed to other unknown high pressure organic syntheses, but on the other hand it has another main theme to elucidate the mechanism of gas phase free radical and atomic reactions, which had been going on also in Kodama Laboratory by Prof. Takezaki in connection with the study of combustion phenomena.

Since then, efforts have been devoted to the exploration of organic synthetic reactions mainly with carbon monoxide under high pressures with the aim of effective utilizations of this industrially important raw material; results have been obtained on "carbonylations" especially with acid catalysts, *e.g.*, glycolic acid, acetic acid, aromatic aldehydes, fatty acids and formamides syntheses *etc.* The character of the research is rather of physico-chemical type, consisting of equilibrium and kinetical studies, but some of them were tested by bench-scale continuous plant for the scale-up. Recently, carbon dioxide has been taken up as a reactant; one example is the synthesis of malonic acid from acetate. Furthermore a gas phase reactor working at 10,000 atm. has been constructed, with which investigations on the polymerization of gaseous compounds and reactions such as water gas reaction or ammonia synthesis are being undertaken.

As to the free radical reactions, kinetical investigations have been made on the mode of attack of methyl, methoxyl, methylene and sulfide radicals, and sulfur or oxygen atoms on the saturated substrates especially containing oxygen.

The techniques of producing radicals are of variety; in addition to pyrolysis and

photolysis (including sensitization), microwave discharge and flash photolysis have been utilized, and recently a study with vacuum ultraviolet light has begun. The methods of observation were generally based on the determinations of final or stable intermediate products by means of gas chromatography, infrared and ultraviolet spectrometry and mass spectrometry along with chemical and electro-chemical micro-analyses and micro-pressure measurements. However, since a time-of-flight mass spectrometer has been installed recently, the determination of radical concentrations during the short reaction time has become possible; by this means the rate constant of an oxygen-atom reaction has been obtained from the steady concentration change within few msec. Further, devices have been developed to see the transient change of atom concentrations with the intervals of 25 μ sec, and combining microwave discharge technique with this, direct measurement of atomic reaction rate is going on.

Publications

(* indicates an article published in Japanese.)

I. Polyethylene Synthesis

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3. Y. Takezaki, N. Okamoto, N. Sugita, S. Yuasa, F. Tanimoto and T. Kawatani: BF_3 Catalyzed High Pressure Synthesis of Acetic Acid from Methanol and Carbon Monoxide, *J. Chem. Soc., Japan, Ind. Chem. Sec.*, **62**, 930 (1959).*
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