

Asymmetric Autocatalysis and Its Role in the Origin of Homochirality

Kenso Soai

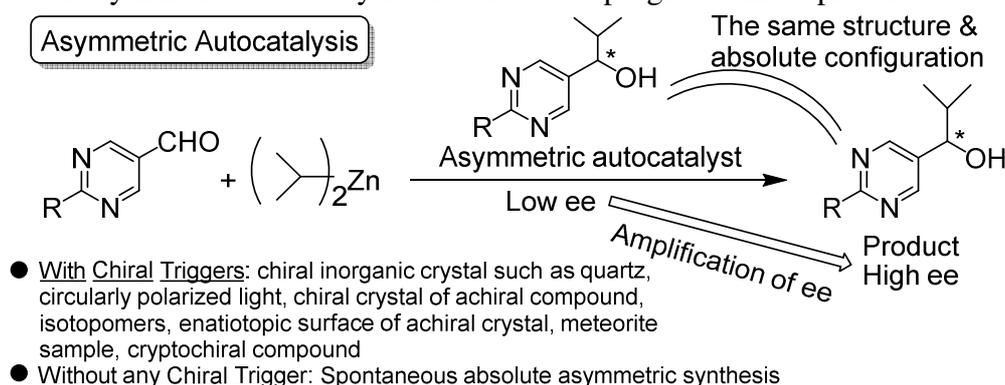
Department of Applied Chemistry, Tokyo University of Science,
Kagurazaka, Shinjuku, Tokyo 162-8601, Japan,

E-mail: soai@rs.kagu.tus.ac.jp

Asymmetric autocatalysis is a reaction in which a chiral product acts as a chiral catalyst for its own production. The process is an automultiplication of chiral molecule, thereby the efficiency is high. Because the product has the same structure and absolute configuration with the catalyst, unlike usual asymmetric catalysis, the amount of catalyst increases and no deterioration of catalyst would be observed in ideal cases. In addition, it is not necessary to separate the product from the catalyst.

In 1995, we found that pyrimidyl alkanol acts as an asymmetric autocatalyst in the enantioselective addition of diisopropylzinc (*i*-Pr₂Zn) to pyrimidine-5-carbaldehyde to afford itself of the same absolute configuration with amplification of enantiomeric excess (ee).¹ The amplification of ee from extremely low to greater than 99.5% ee was achieved by consecutive asymmetric autocatalyses. The amplification of ee was made possible without the need for any other chiral factor than the initial slight imbalance of chirality of asymmetric autocatalyst. The origin and the process leading to the strong one handedness of biological compounds remain as a puzzle for theories of a chemical origin of life. The ees induced by the proposed origin of chirality have been usually very low to moderate.

To take advantage of significant ability of ee amplification, asymmetric autocatalysis of pyrimidyl alkanol with amplification of ee have been applied to examine the proposed origins of chirality: chiral inorganic crystals such as quartz, cinnabar and sodium chlorate, right- and left-circularly polarized light (CPL), chiral crystals formed from achiral organic compounds such as hippuric acid, benzil and tetraphenylethylene, isotopomers,² meteorites, enantiotopic face of achiral crystal, cryptochiral saturated quaternary hydrocarbon was found to work as chiral triggers of asymmetric autocatalysis to afford pyrimidyl alkanol with the absolute configuration correlated to those of chiral triggers. Moreover, spontaneous absolute asymmetric synthesis was achieved in the reaction between pyrimidine-5-carbaldehyde and *i*-Pr₂Zn without the intervention of chiral factor.³⁻⁶ The overview of asymmetric autocatalysis and the recent progress will be presented.



References

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