（アルカリ金属）脱炭酸反応の設計

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Design of (Alkali Metal)decarboxylation Reactions ([1]*Department of Chemistry and Biomolecular Science,* [2]*Department of Materials Chemistry and Processing, Gifu University*)
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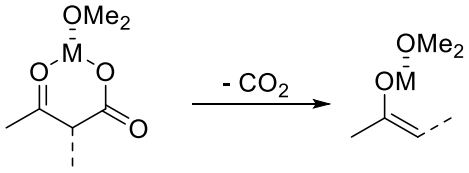

1a: M = Li; **1b**: M = Na; **1c**: M = K

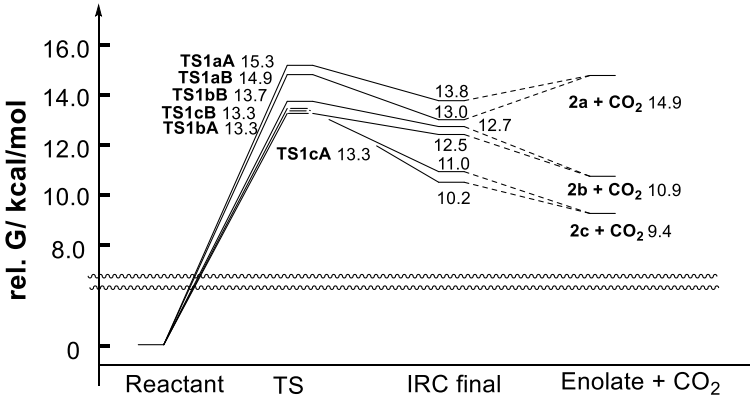

Figure. Reaction coordinates for (alkali metal)decarboxylation.

Decarboxylation reaction is one of the most fundamental reactions in the organic chemistry. All textbooks show that the reaction proceeds with electron movement from $\pi_{C=O}$ to hydrogen. However, the most donating orbital in the carbonyl group should be a lone pair on oxygen, so that the orbital theory perspective should be more appropriate in which the delocalization should occur from the lone pair. We confirmed our idea with the theoretical calculations [1]. Furthermore, we showed that use of boron atom instead of hydrogen led to diastereoselective synthesis of boryl enolate. Here we further investigated the (alkali metal)decarboxylation reaction. Initially, we failed to determine the TSs without solvation. Thus, we performed the calculations including dimethyl ether as a solvent model. We noticed that the reactions are quite endothermic (Fig. 1). Use of potassium α-methyl-*β*-ketocarboxylate resulted in preference of *Z*-enolate formation. Thus, we can expect that treatment of potassium enolates with a tandem carboxylation-decarboxylation sequence would lead to enrichment of *Z*-enolates.

Keywords : (Alkali Metal)decarboxylation; Orbital Theory Perspective; Theoretical Calculation; Endothermic Reaction; Diastereomeric Enrichment

既に当研究室では、脱炭酸反応が教科書にあるカルボニル基の$\pi_{C=O}$軌道からの電子の流れではなく、酸素上の孤立電子対からの非局在化によることを明らかにした。この知見を基に今回、溶媒和した*β*-ケトカルボン酸アルカリ金属塩脱炭酸反応を理論計算によって設計した。反応は非常に吸熱的であり、また、逆反応の活性化エネルギーは非常に小さかった。以前報告したボラ脱炭酸反応とは異なり、*Z*-エノラートの生成が優先する。そのため、低温下でエノラートに二酸化炭素を反応することで、系中で*β*-ケトカルボン酸アルカリ金属塩を発生させ、引き続き昇温することで脱炭酸反応を起こすことで、*Z*-エノラートが濃縮できることが示唆された。

1) Naruse, Y.; Takamori, A.; Oda, K. “Design of Boradecarboxylation Reaction” *ChemRxiv* **2020**, 1-5. doi: 10.26434/chemrxiv.11665728.v1