CARBOXYLATE CATALYSED ISOMERISATION OF UNSATURATED NAC-THIOESTERS

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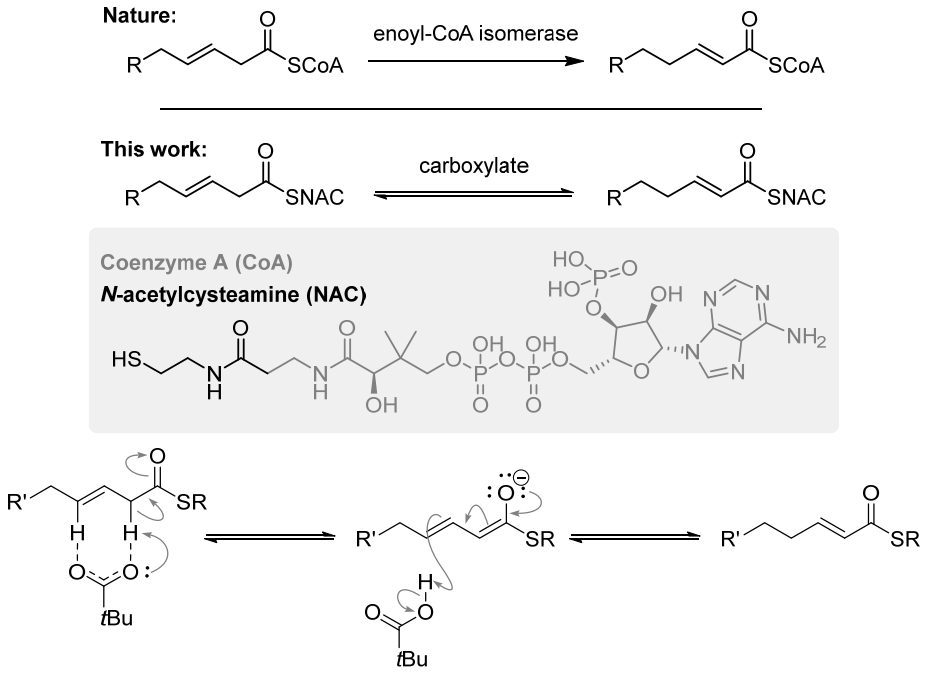
Nature utilizes carboxylates as bases constantly in different enzymatic reactions. For example, the isomerisation of β,γ-unsaturated Coenzyme A thioester is catalyzed by a glutamate residue in the enoyl-CoA-isomerase enzyme.[1] In organic chemistry, carboxylates are commonly considered as weak bases. While this is true in a protic environment, under aprotic conditions – such as in the active pocket of an enzyme or in aprotic solvent – carboxylates can be quite basic.[2]



In this study, simplified version of the isomerisation reaction catalyzed by enoyl-CoA-isomerase has been explored to compare the basicity of two carboxylates to two neutral organic bases. Also, the mechanism of this isomerisation has been studied computationally and experimentally.

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[1] Onwukwe, U. O.; Kursula, P.; Koski, K. M.; Schmitz, W.; Wierenga R. K. *FEBS J.* **2015**, *282*, 746

[2] Kütt, A.; Selberg, S.; Kaljurand, I.; Tshepelevitsh, S.; Heering, A.; Darnell, A.; Kaupmees, K.; Piirsalu, M.; Leito, I. *Tetrahedron.Lett.* **2018**, *59*, 3748