

Revisiting the Kolbe–Schmitt reaction of sodium 2-naphthoxide

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Abstract The mechanism of the carboxylation reaction of sodium 2-naphthoxide (NaphONa) was investigated in the positions 1, 3, and 6 by means of three methods: B3LYP, B3LYP-D2, and M06-2X. While B3LYP failed to describe reaction pathways 3 and 6, B3LYP-D2 (owing to the empirical correction term) and M06-2X (owing to the way it has been parameterised) produced relatively consistent results which create completely new picture of the reaction mechanism. It was found that the reactants can build two NaphONa–CO₂ complexes, of which only one can be further transformed to the reaction products. In this new NaphONa–CO₂ complex, the CO₂ moiety is perfectly positioned to perform electrophilic attacks on all three nucleophilic carbons of the naphthalene ring. Each reaction pathway occurs via two transition states and one intermediate. The mechanism involves a bimolecular reaction step for proton transfer, which requires notably smaller activation barrier than previously considered intramolecular rearrangement. It was shown that reaction pathway 6 is unfavourable from both kinetic and thermodynamic points of view. On the other hand, pathways 1 and 3 are competitive:

pathway 1 requires lower activation barriers, but pathway 3 yields the most stable reaction product. These thermochemical results are in good agreement with the experimentally determined products ratio.

Keywords Carboxylation reaction · Sodium hydroxy naphthoates · Mechanistic study · B3LYP-D2 and M06-2X calculations

1 Introduction

The products of a carboxylation reaction of alkali and alkaline earth metal phenoxides and naphthoxides, called the Kolbe–Schmitt reaction [1, 2], are aromatic hydroxy acids. These compounds have been successfully applied in the production of numerous important chemicals: pharmaceuticals, antiseptics, high-polymeric liquid crystals, polyesters, fungicidal and colour-developing agents, dyes, textile assistants, etc. [3–9]. Due to versatile utilisation of the aromatic hydroxy acids, the Kolbe–Schmitt reaction has been a focus of various experimental and computational researches and is still a vigorous field of investigation. A general outline of the Kolbe–Schmitt reaction of sodium 2-naphthoxide (NaphONa), the subject of the present work, is depicted in Fig. 1.

There are controversial opinions on the Kolbe–Schmitt reaction mechanism. Among several postulations of early researchers, a mechanism involving an intermediate chelate complex between carbon dioxide and metal phenoxide or 2-naphthoxide (MOPh–CO₂ and MONaph–CO₂ where M stands for a metal) is worth emphasising [1, 2, 5, 10, 11]. The presence of the intermediate PhONa–CO₂ complex was confirmed on the basis of the IR absorption spectra [12], as well as FT-IR spectra and DTA analysis [13]. The

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