



Molecular dynamics simulation of the Kolbe-Schmitt carboxylation mechanism of sodium phenoxide

Haodong Zhang^a, Junmei Zhang^b, Wencai Jiang^c, Xuechen Mu^c, Yuanzheng Tang^a, Zhenya Duan^{a,*}

^a College of Electromechanical Engineering, Qingdao University of Science and Technology, Qingdao 266061, China

^b College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

^c Qingdao Dovere Precise Machinery Co., Ltd, Qingdao 266200, China

ARTICLE INFO

Keywords:

Kolbe-Schmitt reaction
Molecular dynamics
Carboxylation mechanism
Density functional theory
Transition state
Intermediate

ABSTRACT

Although we had some understanding of the Kolbe-Schmitt reaction as early as the 21th century, it is surprising that the reaction did not receive sufficient attention through theoretical approaches. The mechanistic underpinnings of the industrially pivotal Kolbe-Schmitt reaction have been the focus of intensive experimental and computational scrutiny. In the present study, we scrutinized the carboxylation of sodium phenoxide with carbon dioxide via density functional theory (DFT) based molecular modeling at the hybrid B3LYP level. Our simulations unveiled that the reaction transpires through three discrete transition states and three discrete intermediates. The last step of the Kolbe-Schmitt reaction is the rate-determining step, as it requires the highest activation energy, which consistent with the experimental results. This concluding step of the Kolbe-Schmitt reaction demands the most substantial activation energy and thus limits the overall rate. This theoretical interrogation has furnished invaluable discernment into the intricacies of the Kolbe-Schmitt mechanism and provides strategic direction for deeper comprehension and optimization of this profoundly applicable carboxylation protocol.

1. Introduction

Carbon dioxide, as a plentiful, renewable, and cost-effective compound, despite its harmful impact on the environment, exhibits tremendous potential in various industrial sectors. Numerous research studies and review articles have been published to further promote carbon dioxide reduction and explore its additional applications (Tor-tajada et al., 2018; Gupta et al., 2022). Among them, the approach of forming C-C bonds is considered an ideal pathway for carbon dioxide utilization due to the higher energy density associated with the newly formed C-C bonds, offering broader prospects for development.

In this regard, carboxylic acid (R-COOH) compounds hold particular importance as they find wide applications in the fields of medicine, pharmaceuticals, chemicals, and other industries (Wu and Zheng, 2018; Gooßen et al., 2008; Rozulan et al., 2022). They serve as model compounds for synthesizing other high-value-added products, thus presenting a captivating direction for the conversion of carbon dioxide. However, a deeper understanding of the carboxylation reaction mechanism, which utilizes CO₂ as a reactant for complete transformation into

new C-C bonds, still requires further in-depth research (Luo and Larrosa, 2017).

The Kolbe-Schmitt reaction is a carboxylation reaction that utilizes alkali metal phenoxides and carbon dioxide as reactants, resulting in the formation of hydroxybenzoic acids (Kolbe, 1860; Kolbe and Lautemann, 1860). This reaction has been widely employed in the industrial production of aromatic carboxylic acids such as salicylic acid, *para*-hydroxybenzoic acid, 3-hydroxy-2-naphthoic acid, and 6-hydroxy-2-naphthoic acid. In this study, we focused on investigating the mechanism of the Kolbe-Schmitt reaction using sodium phenoxide and carbon dioxide as our research subjects.

The mechanism of the Kolbe-Schmitt reaction has been the subject of extensive experimental and theoretical research. In this study, we referred to more recent findings regarding the mechanism of the Kolbe-Schmitt reaction. The work by Kurt et al (Martindale, 1996) provided valuable insights into the mechanism of the Kolbe-Schmitt reaction. Through infrared spectroscopy and differential scanning calorimetry, the existence of the intermediate PhONa-CO₂ complex was confirmed. Furthermore, the study revealed that with increasing temperature

* Corresponding author.

E-mail address: qust_zyduan@163.com (Z. Duan).

<https://doi.org/10.1016/j.ces.2023.119690>

Received 4 October 2023; Received in revised form 25 December 2023; Accepted 27 December 2023

Available online 30 December 2023

0009-2509/© 2023 Published by Elsevier Ltd.