DOI: 10.1002/cphc.201700852

Does Confinement Always Lead to Thermodynamically and/or Kinetically Favorable Reactions? A Case Study using Diels–Alder Reactions within ExBox^{+4} and CB[7]


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The front cover artwork is provided by the group of Prof. Pratim K. Chattaraj (IIT Kharagpur). The image shows a Diels–Alder reaction occurring between 1,3-butadiene and ethylene within ExBox^{+4} and Cucurbit[7]uril. Read the full text of the article at 10.1002/cphc.201700308.

What is the most significant result of this study?

Being able to decipher the role of confinement in affecting the thermodynamic as well as kinetic aspects of a model Diels–Alder reaction. Unlike within ExBox^{+4}, this Diels–Alder reaction is shown to be thermodynamically more spontaneous at 298.15 K and one atmospheric pressure inside CB[7] apart from an increase in the rate of the reaction by several orders of magnitude.

What prompted you to investigate this topic/problem?

Recent experimental advances in supramolecular catalysis motivated us to computationally explore the problem. The confined environment may be effectively made use of to carry out a reaction which is otherwise thermodynamically and/or kinetically not tractable.

What future opportunities do you see (in the light of the results presented in this paper)?

Various rigid macrocyclic host moieties provide ideal platforms to study the effects of confinement on the reactivity of molecules. Further exploration of host–guest systems could not only answer some fundamental queries, but it might turn out to be useful for future experiments and associated industrial requirements. We have shown that confinement can even force a marriage between two unwilling partners like two noble gas atoms. This particular aspect may be adequately exploited by the experimentalists. Moreover, it needs to be seen whether any other state-of-the-art calculation shows that this reaction becomes more favorable inside ExBox^{+4} as well.

Did you expect a very different outcome? If so what was your initial guess?

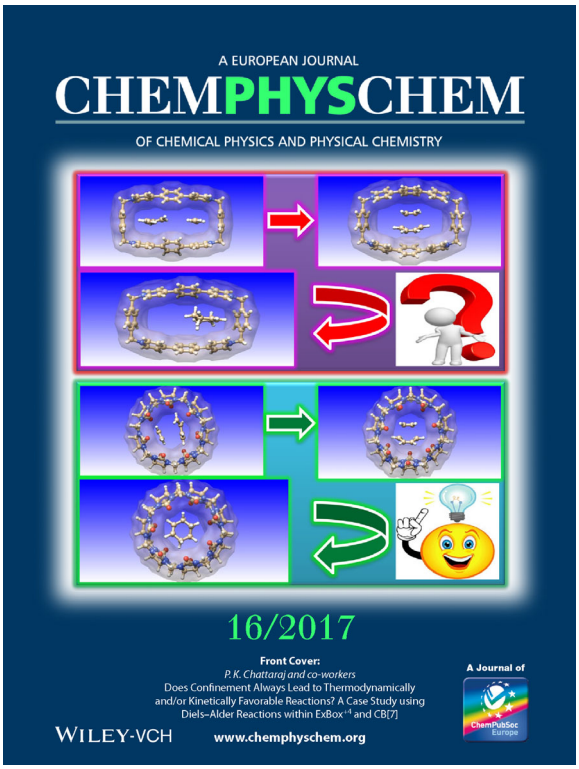
Our initial guess was that the confinement will always lead to thermodynamic and kinetic feasibility of any reaction.

What other topics are you working on at the moment?

The research group of Prof. Chattaraj has been engaged in research on density functional theory, chemical reactivity, hydrogen storage, all-metal aromaticity, nonlinear dynamics, noble gas chemistry, etc.

Acknowledgments

The financial support from Department of Science and Technology, New Delhi, as the JC Bose National Fellowship is gratefully acknowledged by Prof. Chattaraj.



COVER PROFILE

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"The cycloaddition reaction of 1,3-butadiene and ethylene becomes thermodynamically and kinetically more favorable inside cucurbit[7]uril as compared with that inside ExBox^{+4} as well as in the unconfined state…"
This and more about the story behind the front cover can be found in the Full Paper at 10.1002/cphc.201700308.