

Application of DFT models for the prediction of geometries and energies of the transition states in [4+2]- π -electron cycloadditions**Adrianna Falowska^a, Martyna Ząbkowska^a, Karol Sambora^a, Karolina Kula^{a*}, Agnieszka Łapczuk^a and Radomir Jasiński^a**^aCracow University of Technology, Department of Organic Chemistry and Technology, Warszawska 24, 31-155 Cracow, Poland**CHRONICLE***Article history:*

Received April 10, 2025

Received in revised form

June 12, 2025

Accepted October 2, 2025

Available online

October 2, 2025

*Keywords:**Kinetics**Eyring parameters**Secondary kinetic isotope**effects**DFT***ABSTRACT**

The usefulness of various quantum chemical algorithms (semiempirical, HF, DFT) for predicting the energy and geometry of transition states of polar pseudocyclic processes was analyzed using the example of a model cycloaddition process between (Z)-C,N-diphenylnitrone and (E)-2-phenyl-1-nitroethene. These studies clearly recommend the ω B97XD functional in 6-311+G(d) basis set as the relatively most precise tool for studying the mechanisms of polar pseudocyclic processes.

© 2026 by the authors; licensee Growing Science, Canada.

1. Introduction

Ever since the first organic compound was synthesized in the laboratory, scientists have been asking themselves questions about how it was formed. The study of the formation pathway of organic molecules, termed molecular mechanism, quickly became a distinct and crucial field of modern science, straddling organic and physical chemistry¹⁻⁴. Nowadays, a reaction mechanism is defined as a trajectory from substrate to product, through intermediate(s) and transition state(s). Correctly diagnosing the mechanism requires an understanding of the geometric parameters and energies of all critical structures associated with the existence of minima (substrates, products, intermediate(s)) and maxima (transition state(s)) in the reaction energy profile. While studying the geometry of reactants and reaction products existing as stable molecules is straightforward (geometries can be studied using X-ray diffraction^{5, 6} or microwave spectrometry techniques^{7, 8}, while energies can be studied using calorimetric methods⁹), correctly interpreting the chemical properties of intermediates presents a significant challenge. Techniques used for this purpose include trapping intermediates¹⁰⁻¹² with reactive reagents and then analyzing the resulting stable compounds, or real-life analysis using fast spectroscopic techniques¹³⁻¹⁵. Investigating the properties of transition states is an even more challenging task, due to their very short lifespans of approximately 10⁻¹³s¹⁶. Therefore, none of the typical spectroscopic techniques can provide information about the structure or energy of transition states. Some hope for progress in this area can be pinned on the recently reported discoveries in attosecond spectrometry¹⁷. However, at present, there are no tools enabling the practical implementation of this theory in the study of transition states. There is, however, a group of research techniques that allow for the characterization of transition states through indirect methods, without direct observation of the critical structure. In particular, with the ability to measure reaction rate constants, appropriate analyses can be performed at a series of varying temperatures, followed by calculation of activation enthalpies and entropies from the Eyring equation¹⁸. These results, in addition to providing information on the energetics of the transition state, also indirectly provide information on its structure. Large negative entropy changes are typical of transition states of bimolecular processes characterized by a high degree of order, such as cyclic transition states in cycloaddition reactions¹⁹⁻²³. In turn, small activation enthalpies are characteristic of transition states within which changes in the energy

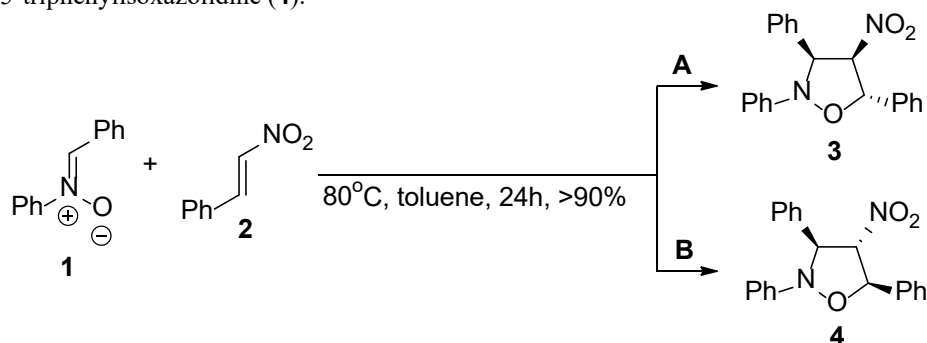
* Corresponding author

E-mail address karolina.kula@pk.edu.pl (A. Falowska)

© 2026 by the authors; licensee Growing Science, Canada

doi: 10.5267/j.ccl.2025.10.001

of the reacting system, determined by the formation of new s-bonds, are compensated by changes resulting from the disintegration of pre-existing p-bonds²⁴⁻²⁷. However, for a while now there has been an available technique that allows one to obtain information on the degree of advancement of new bonds in the transition state^{28, 29}. This technique is based on the measurement of kinetic isotope effects and provides information on the degree of rehybridization at the reaction center, which is closely related to the bond length formed at that atom. We distinguish two types of effects: primary kinetic isotope effects (PKIEs)³⁰ resulting from isotopic substitution of an atom at which new bonds are formed, and secondary kinetic isotope effects (SKIEs)^{31, 32} resulting from isotopic substitution of an atom directly bonded to the atom at which the new bond is formed. Studies of kinetic isotope effects have been used to investigate the mechanisms of many important reactions in organic chemistry³³⁻³⁶. Interestingly, kinetic isotope effects can be easily calculated using quantum chemistry methods utilizing DFT. In this work, we decided to test the usefulness of these methods for predicting activation enthalpies and kinetic isotope effects. For this purpose, we used the (3+2) cycloaddition (32CA) (formally [4+2]- π -electron process) reaction between (Z)-C,N-diphenylnitrone (**1**) and (E)-2-phenyl-1-nitroethene (**2**) as a model process, whose regio- and stereoselectivity has been studied by many groups in the past³⁷⁻⁴⁰. This reaction proceeds with the full regioselectivity and high stereoselectivity yielding the mixture of 3,4-*cis*-3,4-*trans*-4-nitro-2,3,5-triphenylisoxazolidine (**3**) and 3,4-*trans*-3,4-*trans*-4-nitro-2,3,5-triphenylisoxazolidine (**4**).



Scheme 1. Experimental results of the (3+2) cycloaddition reaction between (Z)-C,N-diphenylnitrone (**1**) and (E)-2-phenyl-1-nitroethene (**2**)

For this reaction, we experimentally determined both the activation enthalpies and the SKIE values in our laboratory⁴¹. Within the framework of the present contribution we calculated enthalpies of activation and SKIEs for the nitroalkene substructure based on quantum chemical calculations. This study should enable a comparison of key energetic and structural parameters of the reaction transition states obtained experimentally and theoretically. In convection, this work can also help justify the choice of the level of theory for modeling polar cycloaddition reactions involving both nitroalkenes and other electrophilic components.

2. Results and discussion

First, we compared experimentally measured with quantum chemically estimated Gibbs free activation energy values. As expected, calculations using semiempirical Hamiltonians overestimate the activation barrier so significantly that any attempt to apply such data to the interpretation of practical phenomena is pointless. Intriguingly, the HF⁴² approximation yields even worse predictions of the Gibbs free activation energy. These values are almost twice as high as the realistic ones, even when advanced basis sets are employed. Among DFT methods, the worst approximations are obtained using the old B3LYP^{43, 44} functional, although the overestimations are not as large as in the case of HF calculations. Other functionals underestimate the activation parameters. Calculations using the B97⁴⁵ functional offer a relatively weaker approximation, while the relatively best approximations can be obtained using the ω B97XD⁴⁶ functional. If we compare the influence of basis set on the precision of thermochemical calculations, it is clear that taking into account the diffusion function significantly improves the predictions, bringing the obtained values closer to the actual ones.

Analysis of the suitability of individual levels of theory for predicting SKIEs leads to similar conclusions. Semi-empirical and high-frequency calculations offer results so far removed from reality that the transition state geometries obtained this way are certainly highly distorted and may even lead to erroneous interpretation of the reaction mechanism. In some cases, the estimated SKIE is higher than 1, which makes no physical sense. DFT functionals allow to obtain satisfactory predictions, with the best results achieved using the M062x⁴⁷ and ω B97XD functionals. Visualizations of the transition states of the tested reaction obtained using the latter method in a database with an additional diffusion function are illustrated in **Fig. 1**.

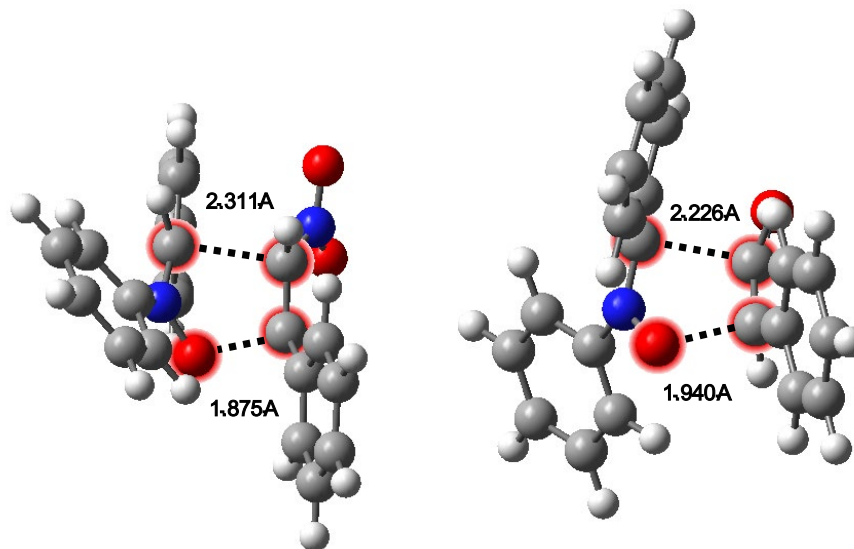


Fig. 1. Views of stereoisomeric transition states for the (3+2) cycloaddition reaction between (Z)-C,N-diphenylnitrone (**1**) and (E)-2-phenyl-1-nitroethene (**2**) according to the ω B97XD/6-311+G(d) (PCM) calculations.

Table 1. Experimental and theoretically predicted key parameters of stereoisomeric transition states for the (3+2) cycloaddition reaction between (Z)-C,N-diphenylnitrone (**1**) and (E)-2-phenyl-1-nitroethene (**2**) (ΔG^\ddagger are in kcal/mol).

Source						
	Path A			Path B		
	ΔG^\ddagger	SKIE ₁	SKIE ₂	ΔG^\ddagger	SKIE ₁	SKIE ₂
Exp. ⁴¹	27.4	0.94	0.92	26.4	0.95	0.92
AM1	42.8	1.02	0.92	42.1	0.99	0.96
PM3	49.1	0.96	0.97	47.8	1.00	0.96
HF/6-311G(d)	49.6	1.06	0.83	46.5	1.04	0.81
HF/6-311+G(d)	50.4	1.05	0.83	47.7	1.04	0.81
HF/def2svp	52.6	0.89	0.96	53.0	0.89	0.87
B3LYP/6-311G(d)	37.8	0.97	0.91	34.5	0.94	0.93
B3LYP/6-311+G(d)	39.7	0.97	0.90	36.6	0.95	0.95
B3LYP/def2svp	35.7	0.97	0.92	33.0	0.94	0.94
B97/6-311G(d)	24.8	0.91	0.93	22.1	0.89	0.96
B97/6-311+G(d)	27.2	0.92	0.93	24.2	0.89	0.94
B97/def2svp	23.2	0.92	0.94	20.7	0.95	0.96
M06/6-311G(d)	26.1	0.97	0.93	23.4	0.93	0.96
M06/def2svp	25.1	0.97	0.94	21.9	0.93	0.97
M062x/6-311G(d)	22.8	0.99	0.91	20.7	0.96	0.92
M062x/def2svp	23.0	0.98	0.92	20.6	0.96	0.93
ω B97XD/6-311G(d)	25.4	0.97	0.89	22.3	0.94	0.92
ω B97XD/6-311+G(d)	27.4	0.97	0.91	23.7	0.94	0.93

3. Computational procedure

All quantum-chemical computations were performed using algorithms implemented in the Gaussian 16 package⁴⁸. The computational PGrid infrastructure at the polish “Cyfronet” centre was utilized. All localized stationary points were verified on the basis of the full vibrational analysis. We found that starting molecules and products had positive Hessian matrices. On the other hand, all optimized transition states (TS) exhibited one negative eigenvalue in their Hessian matrices. Next, the IRC (intrinsic reaction coordinate) trajectories computed for all TSs confirmed, without doubt, their postulated nature and the role within the energy profile. The presence of solvent (toluene) in the reaction environment was included implementing the IEFPCM (Integral Equation Formalism Polarizable Continuum Model) algorithm⁴⁹. Calculations of all critical structures were performed at the temperature $T=353\text{K}$ and pressure $p=1\text{atm}$. Gibbs free energies of the activation and rate constants were calculated using standard thermochemical equations⁵⁰. The kinetic isotope effects were defined as the $k_{\text{H}}/k_{\text{D}}$ ratio. The results are collected in Tables 1.

4. Conclusions

We tested a number of quantum chemistry algorithms that are popular among scientists for their suitability for predicting transition state energies and key transition state parameters. We performed these studies on the test reaction between (Z)-

C,N-diphenylnitrene (**1**) and (E)-2-phenyl-1-nitroethene (**2**). As expected, simpler approaches requiring low computational power provide data so far removed from reality that their use in modeling modern reaction systems is pointless. However, among the DFT functionals tested, the ω B97XD/6-311+G(d) method yielded the best approximation. It is this exact level of theory that we recommend for theoretical studies of the mechanisms of polar pseudocyclic reactions, including cycloadditions.

Acknowledgements

This research was funded in whole by the National Science Centre, Poland, Miniatura 8 (grant number: 2024/08/X/ST4/00933). We gratefully acknowledge Polish high-performance computing infrastructure PLGrid (HPC Centers: ACK Cyfronet AGH) for providing computer facilities and support within computational grant no. PLG/2024/017868.

References

- Chen, S., Babazade, R., Kim, T., Han, S. & Jung, Y. (2024). A large-scale reaction dataset of mechanistic pathways of organic reactions. *Sci. Data*, 11(1), 863. <https://doi.org/10.1038/s41597-024-03709-y>
- Domingo, L. R., Kula, K., Ríos-Gutiérrez, M. & Jasiński, R. (2021). Understanding the Participation of Fluorinated Azomethine Ylides in Carbenoid-Type [3 + 2] Cycloaddition Reactions with Ynal Systems: A Molecular Electron Density Theory Study. *J. Org. Chem.*, 86(18), 12644–12653. <https://doi.org/10.1021/acs.joc.1c01126>
- Sadowski, M. (2024). Alternative Synthetic Protocols as a Way to Mask Unreliability in Organic Chemistry Research, Case of Nitrones. *Sci. Radices*, 3(4), 287–293. <https://doi.org/10.58332/scirad2024v3i4a05>
- Kang, P.-L. & Liu, Z.-P. (2021). Reaction prediction via atomistic simulation: from quantum mechanics to machine learning. *iScience*, 24(1), 102013. <https://doi.org/10.1016/j.isci.2020.102013>
- Łapczuk-Krygier, A., Ponikiewski, Ł. & Jasiński, R. (2014). The crystal structure of (1RS,4RS,5RS,6SR)-5-cyano-5-nitro-6-phenyl-bicyclo[2.2.1]hept-2-ene. *Crystallogr. Rep.*, 59(7), 961–963. <https://doi.org/10.1134/S1063774514070128>
- Takahashi, J. (2023). X-Rays (Organic Synthesis). In *Encyclopedia of Astrobiology*. 3253–3254. Berlin, Heidelberg: Springer Berlin Heidelberg. https://doi.org/10.1007/978-3-662-65093-6_1696
- Gillies, J. Z., Gillies, C. W., Lovas, F. J., Matsumura, K., Suenram, R. D., Kraka, E. & Cremer, D. (1991). Van der Waals complexes of chemically reactive gases: ozone-acetylene. *J. Am. Chem. Soc.*, 113(17), 6408–6415. <https://doi.org/10.1021/ja00017a008>
- Gillies, C. W., Gillies, J. Z., Suenram, R. D., Lovas, F. J., Kraka, E. & Cremer, D. (1991). Van der Waals complexes in 1,3-dipolar cycloaddition reactions: ozone-ethylene. *J. Am. Chem. Soc.*, 113(7), 2412–2421. <https://doi.org/10.1021/ja00007a010>
- Weisenburger, G.A., Barnhart, R. W., Clark, J.D., Dale, D.J., Hawksworth, M., Higginson, P.D., Kang, Y., Knoechel, D.J., Moon, B.S., Shaw, S.M., Taber G.P., Tickner, D. L. (2007). Determination of Reaction Heat: A Comparison of Measurement and Estimation Techniques. *Org. Process Res. Dev.*, 11(6), 1112–1125. <https://doi.org/10.1021/op700173h>
- Jasiński, R. (2015). In the searching for zwitterionic intermediates on reaction paths of [3 + 2] cycloaddition reactions between 2,2,4,4-tetramethyl-3-thiocyclobutanone S-methylide and polymerizable olefins. *RSC Adv.*, 5(122), 101045–101048. <https://doi.org/10.1039/C5RA20747A>
- Suresh, L., Lalrempuia, R., Fjermestad, T., Törnroos, K.W., Bour, J., Frache, G., Nova, A., Le Roux, E. (2025). Trapping of Key “Ate” Intermediates of NHC-Group IV Relevant to Catalyzing Copolymerization of Cyclohexene Oxide with CO₂. *Organometallics*, 44(1), 68–81. <https://doi.org/10.1021/acs.organomet.4c00371>
- Amano, F., Nakayama, S., Suzuki, S., Yamakata, A. & Beppu, K. (2024). Trapping of Intermediates of a Photocatalytic Oxygen Evolution Reaction in Overall Water Splitting. *ACS Appl. Energy Mater.*, 7(4), 1398–1402. <https://doi.org/10.1021/acsaem.3c03172>
- Jodłowski, P.J., Chlebda, D., Piwowarczyk, E., Chrzan, M., Jędrzejczyk, R.J., Sitarz, M., Węgrzynowicz, A., Kołodziej, A., Łojewska, J. (2016). In situ and operando spectroscopic studies of sonically aided catalysts for biogas exhaust abatement. *J. Mol. Struct.*, 1126, 132–140. <https://doi.org/10.1016/j.molstruc.2016.02.039>
- Ronduda, H., Zybert, M., Patkowski, W., Ostrowski, A., Jodłowski, P., Szymański, D., Kępiński, L., Raróg-Pilecka, W. (2021). A high performance barium-promoted cobalt catalyst supported on magnesium–lanthanum mixed oxide for ammonia synthesis. *RSC Adv.*, 11(23), 14218–14228. <https://doi.org/10.1039/D1RA01584B>
- Jodłowski, P. J., Kurowski, G., Dymek, K., Oszałka, M., Piskorz, W., Hyjek, K., ... Sitarz, M. (2023). From crystal phase mixture to pure metal-organic frameworks – Tuning pore and structure properties. *Ultrason. Sonochem.*, 95, 106377. <https://doi.org/10.1016/j.ultsonch.2023.106377>
- Polanyi, J. C. & Zewail, A. H. (1995). Direct Observation of the Transition State. *Acc. Chem. Res.*, 28(3), 119–132. <https://doi.org/10.1021/ar00051a005>
- Maiuri, M., Garavelli, M. & Cerullo, G. (2020). Ultrafast Spectroscopy: State of the Art and Open Challenges. *J. Am. Chem. Soc.*, 142(1), 3–15. <https://doi.org/10.1021/jacs.9b10533>
- Eyring, H. (1935). The Activated Complex in Chemical Reactions. *J. Chem. Phys.*, 3(2), 107–115.

<https://doi.org/10.1063/1.1749604>

19. Zawadzińska-Wrochniak, K., Kula, K., Ríos-Gutiérrez, M., Gostyński, B., Krawczyk, T. & Jasiński, R. (2025). A Comprehensive Study of the Synthesis, Spectral Characteristics, Quantum–Chemical Molecular Electron Density Theory, and In Silico Future Perspective of Novel CBr₃-Functionalized Nitro-2-Isoxazolines Obtained via (3 + 2) Cycloaddition of (E)-3,3,3-Tribo. *Molecules*, 30(10), 2149. <https://doi.org/10.3390/molecules30102149>
20. Sadowski, M., Dresler, E. & Jasiński, R. (2025). On the Question of the Regio-Orientation, Stereo-Orientation and Molecular Mechanism in the Cascade Cycloaddition/Rearrangement/Elimination Processes Leading to Nitro-Substituted Thiopyran Analogs: DFT Computational Study. *Int. J. Mol. Sci.*, 26(18), 8948. <https://doi.org/10.3390/ijms26188948>
21. Kačka-Zych, A., Zeroual, A., Syed, A. & Bahkali, A. H. (2025). Docking Survey, ADME, Toxicological Insights, and Mechanistic Exploration of the Diels–Alder Reaction Between Hexachlorocyclopentadiene and Dichloroethylene. *J. Comput. Chem.*, 46(10). <https://doi.org/10.1002/jcc.70092>
22. Woliński, P., Dresler, E. & Jasiński, R. (2025). A new mechanistic insight into the molecular mechanisms of the addition reactions of 2-aryl-3-nitro-2 H -chromenes to pyrazoles and cyclopentadienes. *New J. Chem.*, 49(20), 8442–8453. <https://doi.org/10.1039/D5NJ01025J>
23. Karaś, A. & Łapczuk, A. (2025). Computational model of the formation of novel nitronorbornene analogs via Diels–Alder process. *React. Kinet. Mech. Catal.*, 138(4), 2671–2689. <https://doi.org/10.1007/s11144-025-02869-1>
24. Wróblewska, A., Sadowski, M. & Jasiński, R. (2024). Selectivity and molecular mechanism of the Au(III)-catalyzed [3+2] cycloaddition reaction between (Z)-C,N-diphenylnitron and nitroethene in the light of the molecular electron density theory computational study. *Chem. Heterocycl. Compd.*, 60(11–12), 639–645. <https://doi.org/10.1007/s10593-025-03387-7>
25. Kula, K. & Jasiński, R. (2024). Synthesis of bis(het)aryl systems via domino reaction involving (2E,4E)-2,5-dinitrohexa-2,4-diene: DFT mechanistic considerations. *Chem. Heterocycl. Compd.*, 60(11–12), 600–610. <https://doi.org/10.1007/s10593-025-03383-x>
26. Aitouna, A.O., Syed, A., Alfagham, A.T., Mazoir, N., de Julián-Ortiz, J.V., Elgorban, A.M., Idrissi, M. El, Wong, L.S., Zeroual, A. (2024). Investigating the chemical reactivity and molecular docking of 2-diazo-3,3,3-trifluoro-1-nitropropane with phenyl methacrylate using computational methods. *Chem. Heterocycl. Compd.*, 60(11–12), 592–599. <https://doi.org/10.1007/s10593-025-03382-y>
27. Ameer, S., Barhoumi, A., Abdallaoui, H.E.A. El, Syed, A., Belghiti, M.E., Elgorban, A.M., Wong, L.S., Wang, S., Idrissi, M. El, Zeroual, A., Mazoir, N. (2024). Molecular docking, exploring diverse selectivities and mechanistic insights in the cycloaddition reaction between 3-benzoylpyrrolo-[1,2-a]quinoxaline-1,2,4(5H)-triones and butyl vinyl ether. *Chem. Heterocycl. Compd.*, 60(11–12), 584–591. <https://doi.org/10.1007/s10593-025-03381-z>
28. Westaway, K. C., Pham, T. Van & Fang, Y. (1997). Using Secondary α Deuterium Kinetic Isotope Effects To Determine the Symmetry of S N 2 Transition States. *J. Am. Chem. Soc.*, 119(16), 3670–3676. <https://doi.org/10.1021/ja962088f>
29. Mao, Z. & Campbell, C. T. (2020). Kinetic Isotope Effects: Interpretation and Prediction Using Degrees of Rate Control. *ACS Catal.*, 10(7), 4181–4192. <https://doi.org/10.1021/acscatal.9b05637>
30. Jasiński, R. (2016). A reexamination of the molecular mechanism of the Diels–Alder reaction between tetrafluoroethene and cyclopentadiene. *React. Kinet. Mech. Catal.*, 119(1), 49–57. <https://doi.org/10.1007/s11144-016-1038-1>
31. Østergaard, L. F. & Hammerum, S. (2021). Secondary kinetic deuterium isotope effects on unimolecular cleavage reactions: Zero-point vibrational energy and qualitative RRKM theory. *Mass Spectrom. Rev.*, 40(6), 821–839. <https://doi.org/10.1002/mas.21660>
32. Storer, J. W., Raimondi, L. & Houk, K. N. (1994). Theoretical Secondary Kinetic Isotope Effects and the Interpretation of Transition State Geometries. 2. The Diels-Alder Reaction Transition State Geometry. *J. Am. Chem. Soc.*, 116(21), 9675–9683. <https://doi.org/10.1021/ja00100a037>
33. Amyes, T. L. & Richard, J. P. (2017). Primary Deuterium Kinetic Isotope Effects From Product Yields: Rationale, Implementation, and Interpretation. 163–177. <https://doi.org/10.1016/bs.mie.2017.06.043>
34. Simmons, E. M. & Hartwig, J. F. (2012). On the Interpretation of Deuterium Kinetic Isotope Effects in C-H Bond Functionalizations by Transition-Metal Complexes. *Angew. Chemie Int. Ed.*, 51(13), 3066–3072. <https://doi.org/10.1002/anie.201107334>
35. Koch, H. F., Dahlberg, D. B., McEntee, M. F. & Klecha, C. J. (1976). Use of kinetic isotope effects in mechanism studies. Anomalous Arrhenius parameters in the study of elimination reactions. *J. Am. Chem. Soc.*, 98(4), 1060–1061. <https://doi.org/10.1021/ja00420a055>
36. Giagou, T. & Meyer, M. P. (2010). Kinetic Isotope Effects in Asymmetric Reactions. *Chem. – A Eur. J.*, 16(35), 10616–10628. <https://doi.org/10.1002/chem.201001018>
37. Boguszewska-Czubarra, A., Kula, K., Wnorowski, A., Biernasiuk, A., Popiołek, Ł., Miodowski, D., Demchuk, O.M., Jasiński, R. (2019). Novel functionalized β -nitrostyrenes: Promising candidates for new antibacterial drugs. *Saudi Pharm. J.*, 27(4), 593–601. <https://doi.org/10.1016/j.jsps.2019.02.007>
38. Ramamoorthy, V., Ramasubbu, A., Muthusubramanian, S. & Sivasubramanian, S. (1999). Pillared Buserite as a new catalytic material for the 1,3-dipolar cycloaddition of α -phenyl-N-(p-methoxyphenyl) nitron with electron deficient olefins. *Synth. Commun.*, 29(1), 21–26. <https://doi.org/10.1080/00397919908085730>
39. Banerji, A., Gupta, M., Biswas, P. K., Prangé, T. & Neuman, A. (2007). 1,3-dipolar cycloadditions. Part XII -

- selective cycloaddition route to 4-nitroisoxazolidine ring systems. *J. Heterocycl. Chem.*, 44(5), 1045–1049. <https://doi.org/10.1002/jhet.5570440511>
40. Joucla, M., Grée, D. & Hamelin, J. (1973). Cycloaddition dipolaire 1,3 sur des composés à liaison éthylenique activée—XVII. *Tetrahedron*, 29(15), 2315–2322. [https://doi.org/10.1016/S0040-4020\(01\)93355-1](https://doi.org/10.1016/S0040-4020(01)93355-1)
41. Jasiński, R. (2004). *Reakcje [2+3] cykloaddycji Z-C,N-difenylnitronu i C,C,N-trifenylnitronu ze sprzężonymi nitroalkenami*. Politechnika Krakowska.
42. Roothaan, C. C. J. (1951). New Developments in Molecular Orbital Theory. *Rev. Mod. Phys.*, 23(2), 69–89. <https://doi.org/10.1103/RevModPhys.23.69>
43. Lee, C., Yang, W. & Parr, R. G. (1988). Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B*, 37(2), 785–789. <https://doi.org/10.1103/PhysRevB.37.785>
44. Becke, A. D. (1993). Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.*, 98(7), 5648–5652. <https://doi.org/10.1063/1.464913>
45. Becke, A. D. (1997). Density-functional thermochemistry. V. Systematic optimization of exchange-correlation functionals. *J. Chem. Phys.*, 107(20), 8554–8560. <https://doi.org/10.1063/1.475007>
46. Chai, J.-D. & Head-Gordon, M. (2008). Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections. *Phys. Chem. Chem. Phys.*, 10(44), 6615. <https://doi.org/10.1039/b810189b>
47. Zhao, Y. & Truhlar, D. G. (2008). The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other function. *Theor. Chem. Acc.*, 120(1–3), 215–241. <https://doi.org/10.1007/s00214-007-0310-x>
48. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Scalmani, G., Barone, V., Petersson, G.A., Nakatsuji, H., Li, X., Caricato, M., Marenich, A.V., Bloino, J., Janesko, B.G., Gomperts, R., Mennucci, B., Hratchian, H.P., Ortiz, J.V., Izmaylov, A.F., Sonnenberg, J.L., Williams-Young, D., Ding, F., Lipparini, F., Egidi, F., Goings, J., Peng, B., Petrone, A., Henderson, T., Ranasinghe, D., Zakrzewski, V.G., Gao, J., Rega, N., Zheng, G., Liang, W., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Throssell, K., Montgomery Jr., J.A., Peralta, J.E., Ogliaro, F., Bearpark, M.J., Heyd, J.J., Brothers, E.N., Kudin, K.N., Staroverov, V.N., Keith, T.A., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A.P., Burant, J.C., Iyengar, S.S., Tomasi, J., Cossi, M., Millam, J.M., Klene, M., Adamo, C., Cammi, R., Ochterski, J.W., Martin, R.L., Morokuma, K., Farkas, O., Foresman, J.B., Fox, D.J. (2016). Gaussian 16, Revision A.03. Gaussian Inc. Wallingford CT.
49. Cossi, M., Rega, N., Scalmani, G. & Barone, V. (2003). Energies, structures, and electronic properties of molecules in solution with the C-PCM solvation model. *J. Comput. Chem.*, 24(6), 669–681. <https://doi.org/10.1002/jcc.10189>
50. Laidler, K. J. (1987). *Chemical Kinetics. 3rd Edition*. Singapore City: Pearson Education.



© 2026 by the authors; licensee Growing Science, Canada. This is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC-BY) license (<http://creativecommons.org/licenses/by/4.0/>).