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lädt ein

gemeinsam mit der Gesellschaft Deutscher Chemiker zum

Vortrag

von Herrn

Prof. J. Philipp Wagner

Institut für Organische und Analytische Chemie

Universität Bremen

“Reactive Intermediates in Molecular Hydrogen Activation *via* Quantum Tunneling”

am: 02. Juli 2026

um: 09:30 Uhr

wo: im Raum A12.232

Gäste sind herzlich willkommen!

TECHNISCHE UNIVERSITÄT
IN DER KULTURHAUPTSTADT EUROPAS
CHEMNITZ

Prof. Dr. Michael Sommer
Telefon: 0371 / 531 32507
E-Mail: michael.sommer@chemie.tu-chemnitz.de

Fakultät für Naturwissenschaften

Institut für Chemie

TUC CHEM
INSTITUT FÜR CHEMIE

Prof. J. Philipp Wagner
Institut für Organische und Analytische Chemie
Universität Bremen

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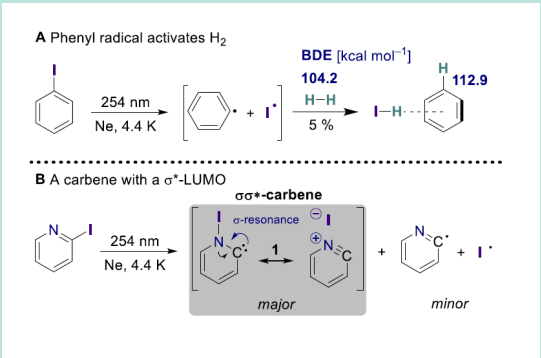
Reactive Intermediates in Molecular Hydrogen Activation *via* Quantum Tunneling

The activation of molecular hydrogen (H_2) poses a significant challenge, that is typically addressed by the utilization of transition metal centers.[1] Main group systems capable of activating dihydrogen have only emerged in the last two decades and rely on cooperative interactions of donor and acceptor orbitals with the antibonding σ* and bonding σ orbitals of dihydrogen, respectively.[2] An alternative method could involve the utilization of (hydrocarbon) radicals, yet the strength of the dihydrogen bond (104.2 kcal mol^{-1}) typically exceeds that of most C−H bonds.[3] We have addressed this challenge by employing the phenyl radical, which reacts with H_2 to form benzene with a high C–H bond dissociation energy (112.9 kcal mol^{-1}), thereby providing a favorable thermodynamic driving force. The hydrogen atom abstraction primarily involves the transfer of a single hydrogen atom, increasing the likelihood of quantum mechanical tunneling to occur.[4] Consequently, upon photolysis of iodobenzene in an H_2-doped neon matrix at 4.4 K, the formation of a benzene−HI complex is observed. Using the heavier D_2 isotopologue leads to the production of phenyl radical, indicating a notable primary kinetic isotope effect.[5] To probe hydrogen activation by the 2-pyridyl radical, 2-iodopyridine was deposited in a solid neon matrix and irradiated with UV light. This unexpectedly yielded a pyridinylidene with an N–I bond, the N-iodo Hammick intermediate. In contrast to conventional carbenes, its lowest unoccupied molecular orbital is the σ* orbital of the heteroatomic bond rather than a π-type orbital, facilitating an unprecedented reactivity. This allows the sideways addition of molecular hydrogen at cryogenic temperatures, revealing a new class of σσ*-carbenes.[6]



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