

Article

Cu(bipy)²⁺/TEMPO-Catalyzed Oxidation of Alcohols: Radical or Nonradical Mechanism?

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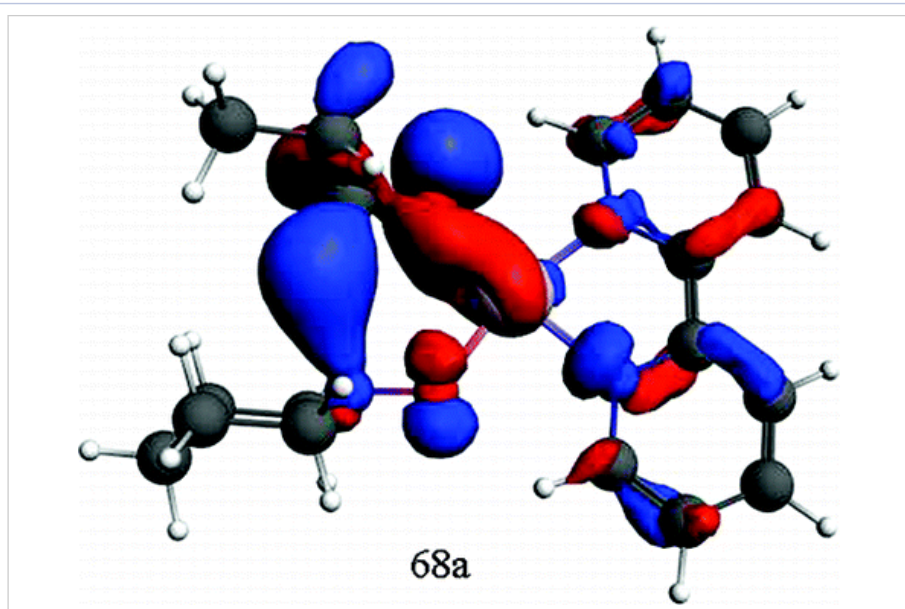
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Abstract



In the oxidation of alcohols with TEMPO as catalyst, the substrate has alternatively been postulated to be oxidized but uncoordinated TEMPO[•] (Semmelhack) or Cu-coordinated TEMPO[•] radical (Sheldon). The reaction with the Cu(bipy)²⁺/TEMPO cocatalyst system has recently been claimed, on the basis of DFT calculations, to not be a radical reaction but to be best viewed as electrophilic attack on the alcohol C-H_α bond by *coordinated* TEMPO[•]. This mechanism combines elements of the Semmelhack mechanism (oxidation of TEMPO to TEMPO[•]) and the Sheldon proposal (“in the coordination sphere of Cu”). The recent proposal has been challenged on the basis of DFT calculations with a different functional, which were reported to lead to a radical mechanism. We carefully examine the results for the two functionals and conclude from both the calculated energetics and from an electronic

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structure analysis that the results of the two DFT functionals are consistent and that both lead to the proposed mechanism with TEMPO not acting as radical but as (coordinated) positive ion.



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