

Time-Resolved Spectroscopic Studies on the Net Heterolysis of Homopolar Selenium-Carbon Bonds

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When thinking about breaking chemical bonds, one considers polarity as the major factor determining if a bond cleavage occurs homolytically or heterolytically, as bonds with a negligible dipole moment tend to undergo homolysis, whereas heterolysis usually requires an electronegative leaving group [1]. We demonstrate for carbon-selenium bonds that in principle this restriction can be circumvented without resorting to the usual means of covalent [2] or hydrogen-bond assisted [3] activation, by utilizing a two-step process. After thermal, homolytic bond cleavage the generated phenylselenenyl radical is selectively excited with visible light and oxidizes its carbon-centered coradical, resulting in an overall net heterolysis of the bond (Figure 1). This process can be utilized for S_N1-type chemistry as well as Friedel-Crafts reactions.

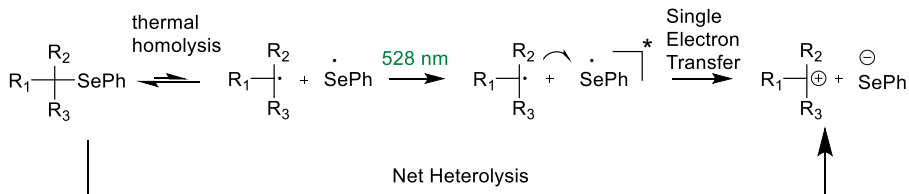


Figure 1: Net Heterolysis of a Carbon-Selenium bond via thermal homolysis followed by light-induced single-electron transfer

The mechanism of this reaction is elaborated through spectroscopic studies of all involved species, including transient absorption spectroscopy [4], as well as theoretical and synthetic investigations.

[1] R. Brueckner, *Reaktionsmechanismen*, Springer Spektrum, 2004.

[2] C. Paulmier, *Phosphorus Sulfur Silicon Relat. Elem.*, 2001, **172**, 25-54, 10.1080/10426500108046638.

[3] S. Park *et al.*, *Angew. Chem. Int. Ed.*, 2022, **61**, e202208611, 10.1002/anie.202208611.

[4] R.J. Kutta *et al.*, *Appl. Phys. B*, 2013, **111**, 203-216, 10.1007/s00340-012-5320-2.