OP-11

HEAVY ATOM TUNNELING, MATRIX EFFECT, AND WAVELENGTH EFFECT IN THE PHOTOREACTION OF 2,3-DIAZABICYCLO[2.2.1]HEPT-2-ENE

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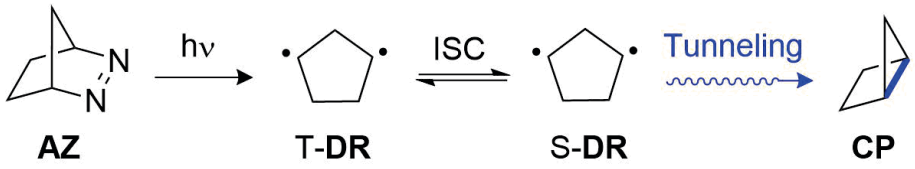
Quantum mechanical tunneling (QMT), recognized as an important phenomenon in chemical reactions, had been studied from mechanistic, kinetic, and theoretical point of view. Hydrogen atom tunneling has been observed in a wide range of chemical reactions in chemistry and biology. Tunneling probability is inversely proportional to the mass of the tunneling particle. Therefore, tunneling reactions involving heavy atoms like carbon (12 times heavier than hydrogen) are rare.

In 1975 and 1979, Buchwalter and Closs directly detected triplet diradical T-**DR** via photolysis of precursor **AZ** and they suggested quantum mechanical tunneling in the decay process of T-**DR**.[1,2] However, the tunneling reaction and product formed after decay of the T-**DR** were not directly characterized. We used low temperature EPR and matrix isolation IR spectroscopy and theoretical calculations to clarify the rate, mechanism, and tunneling process of triplet diradical T-**DR**. Experimental results showed evidence for heavy atom (carbon) tunneling for the formation **CP** from T-**DR** via S-**DR**. The product **CP** formed in the tunneling process was directly characterized using low temperature IR spectroscopy in Ar matrix. We also observed wavelength dependent product distribution in the photolysis of **AZ** at 7 K in Ar matrix. A prominent matrix effect was found as T-**DR** decayed with different rate constants in Ar, glassy 2-methyltetrahydrofuran, and glassy 3-methylpentane matrix.



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[1] S. L. Buchwalter, G. L. Closs, *J. Am. Chem. Soc.* **1975**, *97*, 3857–3858.
[2] S. L. Buchwalter, G. L. Closs, *J. Am. Chem. Soc.* **1979**, *101*, 4688–4694.