Aerobic Nitro-Nitrite Isomerization-Driven Radical Chemistry of Secondary Nitroalkanes

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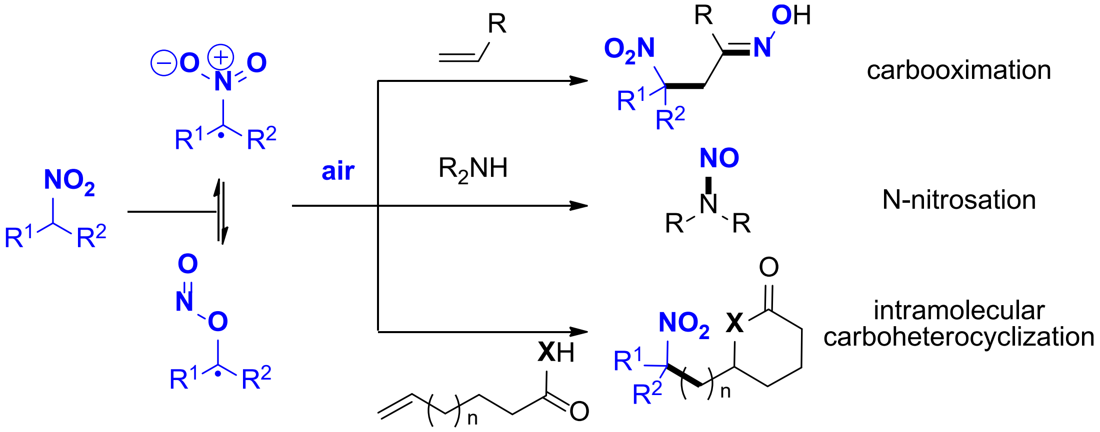
Nitroalkanes are high-energy materials widely employed as fuels and fuel additives due to their favorable bond scission energetics.[1] Despite decades of theoretical and experimental investigation, the decomposition pathways of nitroalkanes remain a subject of ongoing debate.[2] The prevailing theory attributes N–C bond cleavage in nitroalkanes to nitro–nitrite isomerization; however, this mechanism remains contentious, with numerous high-level computational studies failing to provide a definitive resolution.

The synthetic utility of nitroalkanes arises from their facile tautomerization from the nitro form to the *aci*-form, enabling the generation of nucleophilic nitronates under basic conditions.[3] This reactivity has been harnessed in the synthesis of a broad range of compounds, including highly substituted saturated and unsaturated hydrocarbons, amines, and carboxylic acid derivatives. Motivated by the versatility of nitroalkanes as synthetic building blocks, we turned our attention to their decomposition pathways. In contrast to the well-established chemistry of nitronate anions, the corresponding α-nitroalkyl radicals have not been widely recognized as viable intermediates.

In this presentation, we will explore various decomposition pathways of nitroalkanes under aerobic oxidation conditions.[4] Additionally, we will highlight the synthetic applications of nitroalkanes as precursors to both nitrosyl species and α-nitroalkyl radical species.



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