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View Abstract

CURRENT SYMPOSIUM: Coordination Chemistry: Catalysis and Applications

CURRENT SESSION FORMAT: INOR: Oral In-Person

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DIVISION: Division of Inorganic Chemistry (INOR) : I only wish to participate in-person in Washington, DC.

TITLE: Isocyanate synthesis without phosgene: computational and experimental studies for a greener industry

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ABSTRACT BODY:

Abstract: Isocyanates are critical commodity chemicals with multi-million-ton annual production and are traditionally synthesized by reducing nitro compounds into amines, followed by reaction with phosgene.[1] However, phosgene's toxicity and corrosiveness clash with green chemistry principles.[2] Direct reductive carbonylation of nitroarenes has long been proposed as an alternative, yet its mechanism remained unknown, and no practical application has been achieved. [3-4]

Here we propose the first comprehensive mechanism for the direct reductive carbonylation of nitroarenes, aiming to enable viable, efficient synthesis for industrial use. Extensive calculations revealed key intermediates governing the reaction, the rate-determining step, and transition state; while evaluating alternative pathways, potential side reactions and catalyst decomposition routes are proposed. Experimental validation, using reaction kinetics analysis and potential intermediate reactivity studies, confirmed the model's accuracy and limits, offering a robust framework for optimization. Complementary computational methods, including natural bonding orbitals and buried volumes, deepened mechanistic insights of the reaction. We propose alternative conditions, and ligand designs to overcome identified challenges, advancing sustainable isocyanate production.