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REVIEW

Recent Advances in Ammonium Iodide (NH_4I)-Mediated Transformations: Toward Greener and Metal-Free Organic Synthesis

Laxman Mahadev Alakonda[1] | Murali Mohan Achari Kamsali[2] | Mohammed Mujahid Alam[3] | Ravi Varala[4,5,6]

[1]School of Pharmacy, College of Health Sciences, University of Wyoming, Laramie, Wyoming, USA | [2]Department of Chemistry, Sri Venkateswara College, University of Delhi, New Delhi, India | [3]Department of Chemistry, College of Science, King Khalid University, Abha, Saudi Arabia | [4]Scrips Pharma, Mallapur, Hyderabad, India | [5]Research Fellow in Health Sciences, INTI International University, Nilai, Malaysia | [6]Research Fellow, Shinawatra University, Pathum Thani, Thailand

Correspondence: Ravi Varala (ravivarala@gmail.com)

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ABSTRACT

Ammonium iodide (NH_4I) has recently emerged as a versatile and sustainable reagent in modern organic synthesis. This inexpensive and readily available inorganic salt serves as a redox mediator, promoter, and mild iodide source, enabling a broad spectrum of C–C, C–heteroatom, heteroatom–heteroatom, and one-pot multibond-forming reactions under environmentally benign conditions. Its dual functionality as both a nucleophilic iodide donor and an oxidative promoter has facilitated diverse transformations, including oxidative couplings, cyclizations, halogenations, and heterocyclic syntheses. This review provides a comprehensive overview of NH_4I-mediated thermal, photochemical, and electrochemical methodologies reported from 2020 to the present, emphasizing key mechanistic features, reaction scopes, and synthetic applications. By consolidating these recent advancements, this work underscores the growing importance of ammonium iodide as an efficient, green, and metal-free mediator in contemporary organic synthesis and aims to inspire further innovation in sustainable, energy-efficient, and environmentally responsible chemical transformations.

1 | Introduction

Ammonium iodide (NH_4I) is a white crystalline inorganic salt composed of an ammonium cation (NH_4^+) and an iodide anion (I^-) (Figure 1) [1]. It can be conveniently synthesized through the neutralization reaction between hydroiodic acid and ammonia and readily dissolves in water to yield colorless cubic crystals upon crystallization. The compound is also soluble in ethanol and other polar solvents [2]. In aqueous solutions, ammonium iodide exhibits mild acidity due to partial hydrolysis of the ammonium ion, and its vapor pressure increases with temperature. Beyond its laboratory relevance, NH_4I also serves as a dietary supplement to address iodine deficiency-related disorders.

Abbreviations: ACN or CH_3CN or MeCN, Acetonitrile; AIBN, 2,2′-Azobis(2-methylpropionitrile); AcOH, Acetic acid; ARA, Asymmetric reductive amination; $AgSbF_6$, Silver hexafluoroantimonate (V); BHT, Butylated hydroxytoluene; BIM, Bis(indolyl) methane; CDC, Cross-dehydrogenative coupling; DABCO.DCM, 1-(chloromethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium chloride; DCE, Dichloroethane; DCM, Dichloromethane; DFT, Density functional Theory; DGs, Directing groups; DMA, Dimethyl acetamide; DMSO, Dimethyl sulfoxide; DMF, Dimethylformamide; EDG, Electron donating group; EWG, Electron withdrawing group; $g\text{-}C_3N_4$, Graphitic carbon nitride; GC, Graphite charcoal; HMDS, Hexamethyldisilazane; HI, Hydroiodic acid; KI, Potassium iodide; LED, Light emitting diode; LiCl, Lithium chloride; LiI, Lithium iodide; *m*CPBA, *meta*-Chloroperoxybenzoic acid; NaI, Sodium iodide; NBS, *N*-Bromosuccinimide; ND, Not detected; NR, No reaction; NIS, *N*-Iodosuccinimide; NH_4Br, Ammonium bromide; NH_4I, Ammonium iodide; NMP, *N*-Methyl-2-pyrrolidone; Oxone, Potassium peroxymonosulfate; PCR, Polymer chain reaction; PIDA, Phenyliodine (III) diacetate or (diacetoxyiodo)benzene; SET, Single electron transfer; TBAI, Tetrabutyl ammonium iodide; TBHP, *tert*-butyl hydroperoxide; TMS, Trimethylsilyl; TMSI, Trimethylsilyl iodide; THAI, Tetrahexylammonium iodide.

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