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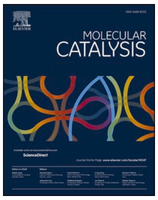

Facile dehydration of primary amides to nitriles catalyzed by lead salts: The anionic ligand matters

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ABSTRACT

The synthesis of nitrile under mild conditions was achieved via dehydration of primary amide using lead salts as catalyst. The reaction processes were intensified by not only adding surfactant but also continuously removing the only by-product, water from the system. Both aliphatic and aromatic nitriles can be prepared in this manner with moderate to excellent yields. The reaction mechanisms were obtained with high-level quantum chemical calculations, and the crucial role the anionic ligand plays in the transformations were revealed.

1. Introduction

Nitriles constitutes an important class of raw materials or intermediates that are widely employed in the production of polyamides, pharmaceuticals, agrochemicals, dyes, pigments, and various fine chemicals for their unique reactivity [1–5]. As the most known example, adiponitrile is used to produce hexamethylene diamine, the raw material of polyamide fiber [6–8]. In the past decades, various studies have been reported for the synthesis of nitriles. Originally, stoichiometric methods prevailed in both laboratories and industry, including Rosenmund-von Braun reaction of aryl halides [9,10]. Schmidt reaction of aldehydes [11], the diazotization of anilines with subsequent Sandmeyer reaction [12], etc. However, due to (over) stoichiometric amounts of the dehydration reagents used, the same amounts of wastes are produced. Ammoxidation of olefins or alkanes seems to be a more sustainable method, in which the olefins or alkanes react with oxygen and ammonia at 300−550 °C in the presence of a heterogeneous fixed-bed catalyst [13–18]. However, this method is limited by harsh reaction conditions.

To obtain a facile method to produce nitriles, great efforts have been made in developing more efficient catalytic systems [19–28]. The dehydration of amides turns out to be a promising route to prepare the corresponding nitriles [29]. However, classic dehydration of amides was implemented using stoichiometric or excessive amount of dehydrants, such as $SOCl_2$ [30], P_2O_5 [31] $POCl_3$ [32], $TiCl_4$ [33], $NaBH_4$ [34], $EtOP(O)Cl_2$ [35], benzensulfonyl chloride [36], and trichloroacetyl chloride [37]. Unfortunately, these hydrants react with water to afford stochemical pollutional species. Both the laboratory and the industry needs facile and clean dehydration of amides! Recent efforts on this topic focus on catalytic dehydration of amides in the presence of hydrosilane. The catalysts used are typically transition metals [38–52] or metal-free species [53,54]. Though these methods permit the reaction to proceed under neutral, mild conditions, stoichiometric dehydrants are still required. Shi and coworkers [55] reported Pd-catalyzed decarbonylative cyanation of amides to produce aryl nitriles – an important improvement, while this protocol is not available for the synthesis of alkyl nitriles. Herein, we report a facile, simple protocol for the dehydration of amides catalyzed by lead salts without using any dehydrant. It will be shown later that the anionic component of the lead salt is crucial for the reaction efficiency. The reaction mechanisms and the origins for the experimental findings are revealed with quantum chemical calculations.

2. Results and discussion

The dehydration of butanamide was chosen as the model reaction to screening the reaction parameters (Scheme 1). The results are detailed in Table 1.

To start with, the experiments were conducted in different solvents (entries 1–6, Table 1). When the reaction was carried out in the hydrophilic solvent such as methanol (entry 1, Table 1), acetonitrile (entry

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