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Review

Metal-mediated and metal-catalyzed hydrolysis of nitriles

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Abstract

The essential goals of this review are the following: (*i*) to verify various factors which affect the metal-mediated hydrolysis of organonitriles; (*ii*) to draw attention to unusual conversions of RCN species, yet underdeveloped and non-systematic, which involve hydrolysis and lead to compounds of synthetic and/or pharmacological significance. The metal-mediated and/or metal-catalyzed reactions of RCN species are surveyed and the experimental material on metal-mediated hydration of RCN species at diverse metal centers along the Periodic Table is summarized in a tabular form.

Vadim Yurievich Kukushkin, Full Professor at St.Petersburg State University; for excellence in teaching he was awarded a Soros Professorship in 2001–2004. In 2003, he was appointed as a new Editorial Board member of Inorganica Chimica Acta representing the Russian Federation. He also an Editorial Board member of the Russian Journal of General Chemistry and Executive Secretary of the General and Inorganic Chemistry Section of the Russian Chemical Society. Published ca. 170 original research papers, patents, reviews and 4 books. Research interests: platinum group metal chemistry, ligand reactivity, activation of small molecules, and organic synthesis involving metal complexes.

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Since its inception in 1994, the collaboration between the two authors and their respective teams has resulted in 50 joint publications, a figure which ably demonstrates the successful nature of this international cooperation. We trust that if the dissolution of political borders remains ongoing and the integration between the former Eastern bloc countries and the West continues then they will turn out to be only the first fifty of many more.

Contents

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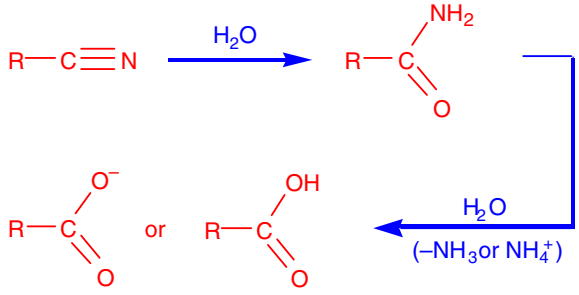
1. Introduction

The *hydrolysis*, i.e., splitting with water, or the *hydration*, i.e., addition of water, (both terms are normally used here as synonyms) of nitriles is an area of great synthetic significance for the preparation of amides (e.g., acrylamide or nicotineamide) and carboxylic acids (e.g., *R*-(−)-mandelic acid and *S*-(+)-ibuprofen) in view of the industrial applications and pharmacological interest of both classes of these compounds. This reaction proceeds in the distinct steps under acid or base treatment (Scheme 1):



Scheme 1.

The hydrolysis of nitriles is generally considered to be one of the best methods for the preparation of carboxylic acids. However, these base or acid catalyzed reactions have certain limitations and/or disadvantages for preparation of amides. The general restriction is that the final neutralization of either base or acid leads to an extensive salt formation with inconvenient product contamination and pollution effects [1,2]. Particular limitations are as follows: (i) *The base catalyzed reactions.* The kinetic studies allowed the estimate of relative rates for the hydration at each step of the reaction and, as a typical example, the second-order rate constants for hydroxide-ion catalyzed hydrolysis of acetonitrile and acetamide are 1.6×10^{-6} and 7.4×10^{-5} M^{-1} s^{-1}, respectively [3]. Comparison of these two values indicates that the second step of the hydrolysis for the base-catalyzed reaction is faster than the first one, and the reaction should proceed to the final hydration product (the carboxylate salt) rather than stopping at the amide stage [2,4]. This implies that amides prepared in the conven-

Abbreviations: Me, methyl; Et, ethyl; Pr, propyl; Bu, butyl; Ph, phenyl; Ar, aryl; Cp, cyclopentadienyl; cod, 1,5-cyclooctadiene; PzH, pyrazole; acac, acetylacetonate; dppe, 1,2-bis(diphenylphosphino)-ethane; en, ethylenediamine; py, pyridine; tpy, 2,2′:6′2″-terpyridine; bpy, 2,2′-bipyridine; DME, dimethoxyethane; THF, tetrahydrofurane; HOAc, acetic acid.