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Proton transfer in the solid state: Reactions of organic acids and amines

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Abstract

Grinding of crystalline organic acids and amines leads to proton transfer with ammonium salt formation or to hydrogen bonded complexes. Formation of amides is not achieved with these reagents even under strong impact. The mechanochemical processes were monitored by IR spectroscopy. Thirteen acids and four amines covering a wide range of acidity, basicity and hardness were employed.

Keywords: Mechanochemistry; Ammonium salts

1. Introduction

The interactions of organic acids and amines have been widely studied in solutions or in molten phases [1,2]. Salt formation with proton transfer from the acid to the amine takes place readily with very low activation energy [3]. Attack of the amine to the carbonyl carbon leads to amide formation, but this process has a high activation energy and requires elevated temperatures [2].

Grinding of solid organic acids and amines could lead to these reactions as well as to hydrogen bonded complexes and solid solutions. Mechanochemical reactions are attractive since they are simple, avoid the use of solvents and do not contaminate the environment [4–6].

In this report we present our results of mechanochemical reactions of 13 crystalline organic acids of very different acidity (K_a from 10^{-2} to 10^{-5}) and 4 solid amines (K_b from 10^{-4} to 10^{-12}) with a wide range of hardness (melting points from 45 to 250°C).

The reactions have been monitored by IR spectroscopy which enables the identification of the products in the solid reaction mixture.

2. Experimental

2.1. Reagents and standards

The 13 organic acids and 4 amines employed were analytical grade commercial products. The IR spectra confirmed their purity. The salts were obtained by mixing ethanolic solutions of the acid and the amine in stoichiometric quantities and allowing the solution to crystallize. With weak acids and bases the salt is

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