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Proton transfer in the solid state: mechanochemical reactions of fluorides with acidic substances

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Abstract

Crystalline KF reacts with solid acidic substances by milling in an agate mortar. Proton transfer takes place between the acid and KF with formation of KHF_2 and the K salt of the acid. The reactions were monitored by IR and XRD techniques in the solid reaction mixture. The following substances react readily with KF: $KHSO_4$, KH_2PO_4, $(NH_4)_2SO_4$, and organic acids (oxalic, maleic, benzoic, *p*-chlorobenzoic, p-nitrobenzoic, miristic and nicotinic). NH_4F, NaF are less reactive in that order while LiF and CaF_2 are inert.

1. Introduction

Proton transfer between an acid and a base has been exhaustively studied in gaseous and liquid phases but scarcely in the solid state [1,2]. We have recently shown that organic acids and amines can react by milling the crystalline reagents in a mortar, to form ammonium salts [3]. The most common basic systems are those of nitrogen and oxygen derivatives like oxides, hydroxides and amines.

Fluorides also have basic properties and have been used as catalysts in organic reactions for this reason [4]. Due to this basicity of F^-, the acid bifluoride anion HF_2^- is a very stable hydrogen bonded complex [5,6]. This anion is present in HF [7,8] and acid fluorides such as KHF_2 [9–13], $NaHF_2$ [14], NH_4HF_2 [15], $LiHF_2$ [16] and $TlHF_2$ [17]. The basicity of the fluorides depends on the nature of the gegen ion in the order $Cs > Rb > K > Na > Li$ [5,17].

In this paper we present a novel mechanochemical process: the deprotonation of acidic substances by KF in the solid state, leading to the formation of KHF_2 and the K salt of the acid. The reactivity of other fluorides like NaF, LiF, NH_4F, and CaF_2 were also studied. The reactions were monitored by IR and XRD techniques.

2. Experimental

All the acidic reagents and fluorides used in the reactions were analytical grade commercial products. The K salts of the organic acids which were used as standards for IR, were synthesized in the laboratory neutralizing equimolar ethanolic solutions of the acid

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