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Mechanochemical reactions of telluric acid with alkaline fluorides

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Abstract

The mechanochemical reactions of telluric acid, $Te(OH)_6$ with alkaline fluorides (Na and K) have been studied using IR and XRD techniques. The reactions lead to the formation of hydrogen-bonding complexes, $NaF.Te(OH)_6$ and $2KF.Te(OH)_6$. The reactions are free from side products such as alkali tellurates, alkali fluorotellurates or HF_2^- salts.

Keywords: Telluric acid; Brönsted acids; Alkaline halides

1. Introduction

Ionic fluorides are widely used as basic reagents in organic chemistry [1] and fluoride ion affinities provide a novel scale for Lewis acidities [2]. With Brönsted acids the fluoride anion is capable of subtracting a proton, forming the very stable acid difluoride anion HF_2^- [3]. In the solid state, even weak acids such as nicotinic ($K_a = 1.4 \times 10^{-5}$) react mechanochemically with KF to form K nicotinate and KHF_2 [4].

$$2KF + RCO_2H \rightarrow RCO_2K + KHF_2 \quad (1)$$

Telluric acid, $Te(OH)_6$, is a very weak Brönsted acid ($K_{a1} = 2.09 \times 10^{-9}$, $K_{a2} = 6.46 \times 10^{-12}$). Its reactions with soluble fluorides have been studied in water solutions. With aqueous HF, the reaction leads to the successive substitution of $(OH)^-$ groups by F^-, forming the whole series of fluorotelluric acids $Te(OH)_{6-x}F_x$ up to TeF_6 [5]. The hexafluoride can be hydrolyzed slowly in water giving the fluorotelluric acids in reverse order down to $Te(OH)_6$ [6].

A water solution of telluric acid can react with solutions of NaF and KF giving crystalline complexes in which the F^- anion is hydrogen-bonded to three hydroxyl protons [7,8]. The stoichiometries are $NaF{\cdot}Te(OH)_6$ and $2KF{\cdot}Te(OH)_6$.

The reactions of telluric acid with alkali fluorides in the solid state have not been reported. Three different courses for the mechanochemical reactions can be envisaged.

1. Formation of the hydrogen bonding (HB) complexes as in water solution [7,8].
2. Subtraction of acidic protons with formation of acid difluoride alkali salts and alkali tellurates [4].
3. Ligand substitution of $(OH)^-$ for F^- leading to fluorotelluric acids or the alkaline salts.

We have performed mechanochemical reactions of crystalline telluric acid with solid NaF and KF in an agate mortar, monitoring the reactions by XRD and IR techniques. The results indicate an efficient reaction of type 1 with no side products, leading to the HB complexes.

2. Experimental

The chemicals telluric acid, NaF and KF were analytical grade reagents from BDH and SIGMA. The milling of telluric acid with alkaline halides in proper molecular ratios was carried out by hand in an agate mortar for 10–20 m. The milled paste was left to stand in desiccators at 50 °C.

The samples were analyzed by XRD and IR using a D-8 advance diffractometer (from Bruker) and an Equinox 55 FTIR spectrophotometer (also from Bruker), respectively. The IR spectra were run in KBr pressed disks, milling first the KBr and gently milling the sample with the matrix to avoid mechanochemical reactions [4].

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