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Proton Transfer in Solid State: Mechanochemical Reactions of Imidazole with Metallic Oxides

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Mechanochemical reactions of crystalline imidazole with 23 metallic oxides have been studied by milling in a mortar and in ball mill vibrators of low and high mechanical intensity. The reactions were monitored by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) techniques. ZnO, HgO, Ag_2O, and Cu_2O react rather readily in the mortar, forming the corresponding imidazolates but CdO, Ga_2O_3, and In_2O_3 require intense mechanical milling to transform. CuO and NiO do not react immediately but turn bluish after a few months of aging. The oxides of Mg(II), Ca(II), Be(II), Al(III), Fe(II), Co(II), Co(III), Pb(II), Eu(III), Ce(III), Bi(III), Ti(IV), Zr(IV), and Sn(IV) are inert to imidazole even on strong milling for several hours.

INTRODUCTION

Imidazole (ImH) is a nitrogen heterocycle of paramount biological importance. As part of the hystidine molecule it constitutes the binding site of transition metal cations in metalloproteins (1, 2). Another important role of the imidazole moiety is as a proton transfer agent in living systems (3, 4). These remarkable properties are due to its molecular structure, which allows imidazole to act as a weak acid and as a strong base (2, 5) (see Fig. 1). In neutral solutions the main species in equilibria are the neutral

These reactions have always been carried out drophilic solvents (2). A lot of theoretical work in transfer and cation complexing has been published r (12–14). Scheiner and Yi (13) have studied the proton fer between imidazole and ammonia and the proton ling between imidazole molecules. Bredas *et al.* (1 studied the electronic structure of hydrogen b imidazole chains, obtaining that the conductivity of c line imidazole is protonic. Basch *et al.* (12) has calcula effect of Na^+ and Zn^{+2} binding on the ionizat imidazole dimers.

Mechanochemical reactions of imidazole have no explored. In this report we study the interactions of c line imidazole with solid metallic oxides by grind a mortar and in ball millers. In most cases the oxic inert but a few react to produce imidazolates. The soli mixtures were studied by infrared (IR) and X-ray diffr (XRD) techniques.

EXPERIMENTAL

All reagents were analytical grade commercial pr The samples were ground in an agate mortar for 30 min, in a light stainless steel ball mill of the wigg