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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. © 1999 Academic Press

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 molecule (ImH) and the protonated imidazolium cation $(ImH_2)^+$ ($pK_a = 7.0$), while in strongly alkaline solutions ImH ionizes to form the imidazolate anion $(Im)^-$ ($pK_a = 14.4$) (6). The imidazole molecule can complex transition metal cations in neutral solutions or form insoluble imidazolates in basic media (7–11). For example:

$$2(ImH) + Zn^{2+} \rightarrow (ImH)_2Zn^{2+} \quad [1]$$

$$2(Im)^- + Zn^{2+} \rightarrow (Im)_2Zn. \quad [2]$$

These reactions have always been carried out in hydrophilic solvents (2). A lot of theoretical work in proton transfer and cation complexing has been published recently (12–14). Scheiner and Yi (13) have studied the proton transfer between imidazole and ammonia and the proton shuttling between imidazole molecules. Bredas *et al.* (14) has studied the electronic structure of hydrogen bonded imidazole chains, obtaining that the conductivity of crystalline imidazole is protonic. Basch *et al.* (12) has calculated the effect of Na^+ and Zn^{+2} binding on the ionization of imidazole dimers.

Mechanochemical reactions of imidazole have not been explored. In this report we study the interactions of crystalline imidazole with solid metallic oxides by grinding in a mortar and in ball millers. In most cases the oxides are inert but a few react to produce imidazolates. The solid state mixtures were studied by infrared (IR) and X-ray diffraction (XRD) techniques.

EXPERIMENTAL

All reagents were analytical grade commercial products. The samples were ground in an agate mortar for 15 to 30 min, in a light stainless steel ball mill of the wiggle-bug type for 30 min, and in a heavy high energy ball mill (Spex 8000) for 1 to 3 h. The solid reaction mixtures were analyzed by FTIR and XRD. A Nicolet FT-IR spectrometer was used. Most of the samples were run in KBr pressed disks except those of Cu, Ag, and Hg which were run in Nujol mulls to avoid reactions of the cations with the KBr matrix (15, 16).

XRD patterns were run in a Siemens D-5000 diffractometer, using Cu$K\alpha$ radiation. Standard samples of imidazolates were obtained by adding a soluble salt of the cation to an excess solution of imidazole at pH 11.0, filtering, washing, and drying the precipitate in a desiccator. Their purity was checked by IR and XRD.

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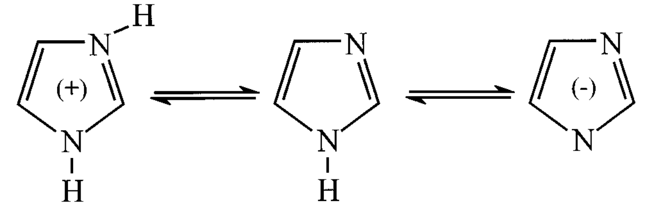

FIG. 1. Imidazole and its ions. (a) Imidazolinium cation, ImH_2^+; (b) imidazole, ImH; (c) imidazolate anion, Im^-.

RESULTS AND DISCUSSIONS

A. Characterization of Imidazole and Imidazolates

Imidazole has a peculiar IR spectrum in solid state (see Fig. 2 and Table 1). The NH stretch, instead of being a narrow band in the 3300 cm^{-1} region, is a very intense broad absorption from 3000 to 2500 cm^{-1}. The broad band is due to the vibrations of the strong H bridges between the pyrrolic N1 and the pyridinic N3 nitrogens. The band is modulated to produce five maxima, due to Fermi resonance interactions of ν_{NH} with forbidden bands (harmonics and combination bands) leading to Evans windows (10, 13–15, 17–20).

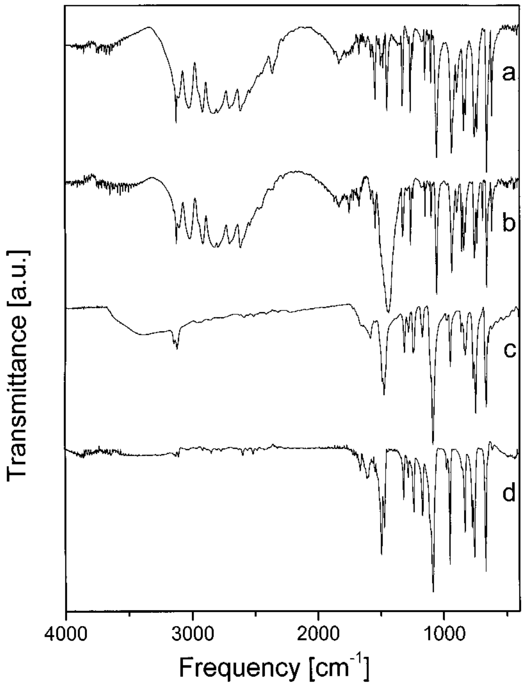

FIG. 2. Total IR spectra (4000–400 cm^{-1}) of: (a) Imidazole (ImH); (b) mixture of ImH and BaO after prolonged milling; (c) mechanochemical reaction of ImH + Cu_2O; (d) mechanochemical reaction of ImH + ZnO. Note the changes in the region of NH stretching vibrations of ImH for those metal oxides that react with Imidazole on milling.

TABLE 1
Analytical Infrared Bands Used to Monitor the Reaction between Metal Oxides and Imidazole

Band assignment	Imidazole (cm^{-1})	Imidazolate (cm^{-1})
NH stretch	3000–2500	None
NH bend	1540	None
NH bend	1147	None
CH bend	1055	1083–1087
CH bend	937	952
Ring torsion	660	672
Ring torsion	620	—
Metal-N stretch	None	~300–400

When imidazole reacts with the oxides, this broad NH band disappears (see Fig. 2). Also, the sharp intense band at 1055 cm^{-1} corresponding to a CH bending vibration, shifts to 1085 cm^{-1} on proton transfer (10) (see Fig. 3 and

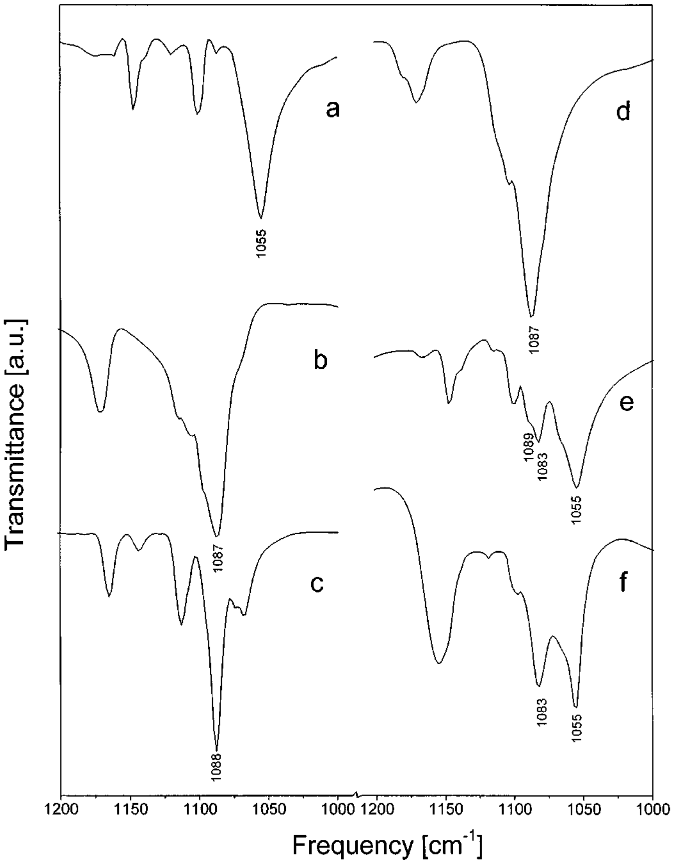

FIG. 3. IR spectra in the range of δ_{CH} vibrations of: (a) imidazole (ImH) (1055 cm^{-1}); (b) Im_2Zn (1087 cm^{-1}); (c) Im_2Cd (1088 cm^{-1}); (d) ImCu (1087 cm^{-1}); (e) mixture of ImCu and imidazole (from the mechanochemical reaction of ImH with CuO 1 year old) (1089, 1083, 1055 cm^{-1}). (d) Mixture of Im_3In and Imidazole (from the incomplete reaction of imidazole with In_2O_3) (1083, 1055 cm^{-1}).

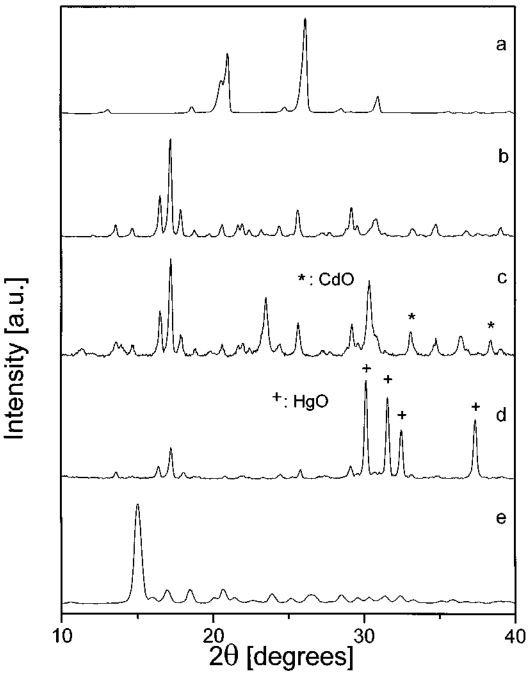

FIG. 4. XRD powder patterns of: (a) imidazole (ImH); (b) Im_2Cd obtained from basic aqueous solution of $CdCl_2$ and ImH; (c) Im_2Cd from the mechanochemical reaction of CdO and ImH; (d) Im_2Hg from the mechanochemical reaction of HgO and ImH; (e) Im_2Zn from the mechanochemical reaction of ZnO and ImH. For simplicity, the excess of ImH in (c), (d), and (e) was removed by washing with distilled water.

Table 1). XRD is also a powerful technique for following the mechanochemical reactions by the disappearance of the imidazole and oxide reflections, which are strong in the diffraction pattern and the appearance of reflections of the imidazolate at lower 2θ values (see Fig. 4).

Imidazolates are normally insoluble polymeric materials with chain, planar, or tridimensional structures depending on the valence of the cation. Zn and Co are tetrahedrally coordinated while Cu and Ni form square planar complexes. Three different forms have been described for Cu^{2+} imidazolate. This polymorphic behavior is widespread (21, 22).

However, imidazolates have the peculiarity of presenting polymorphism (21, 22). As we can see in Fig. 4, depending on the synthetic path, the XRD of the imidazolate product changes while the IR spectra remains unchanged (see Figs. 2–4).

B. Reactive Oxides

Of the 23 oxides studied, only 4 react rapidly on grinding by hand: ZnO, HgO, Ag_2O, and Cu_2O. Three more, CdO, Ga_2O_3, and In_2O_3, react slowly on grinding in the high impact Spex 8000 miller. All lead to imidazolates (see Figs. 2–4).

C. Unreactive Oxides

The oxides of divalent Mg, Ca, Ba, Co, Pb, Ni, and Cu, trivalent Al, Fe, Co, Eu, Ce, and Bi and tetravalent Ti, Zr, and Sn are inert toward imidazole. In the cases of Cu(II) and Ni(II), they transform on aging, the milled samples becoming bluish with time. The mechanism in the case of CuO must be the slow transformation of CuO to Cu_2O, which then reacts rapidly with imidazole (see Fig. 3).

D. On the Mechanism of Reaction of Imidazole with Metal Oxides

The mechanochemical reaction of ZnO and imidazole is most remarkable. A soft solid like imidazole can disrupt the highly cohesive crystals of ZnO with a melting point of 1975°C by mere hand milling. If the mixture is stoichiometric the reaction is almost complete in 30 min. If excess oxide is used, the imidazole IR bands disappear in 5 min but if imidazole is in excess, the oxide band at low frequency remains for almost 1 h. The slowness of the reaction in the last case is due to the dispersion of the hard grains of ZnO in a soft media and the mechanical energy is expended in low-energy collisions within the imidazole. When ZnO is in excess, the majority of the collisions are high energy ZnO ones (23). PbO, a soft material which has a melting point of 886°C, is not attacked by imidazole even after 2 h in the Spex miller. There is no apparent correlation between hardness of the oxide and its reactivity toward imidazole.

Since the mechanochemical process of imidazolate formation requires the deprotonation of N1 to form the imidazolate anion, the basicity of the oxide should be an important factor in this reactivity. However, the most basic oxides such as MgO, CaO, BaO, and Al_2O_3 are all inert.

The common factor among the reactive oxides is the ability of the metal to form strong complexes with N compounds (2). It is also known that complexation increases the acidity of imidazole in solution, lowering its pK_a from 14 to 12 (24). These facts indicate that the deprotonation of N1 is preceded by the complexation of the metal cation by N3 which increases the acidity of imidazole and leads to deprotonation of N1:

$$Zn^{2+} + (ImH) \rightarrow Zn\ldots(ImH)^{2+} \rightarrow (ZnIm)^{1+} + H^{+}. \qquad [3]$$

The process is further enhanced by the binding of the expelled proton by another basic entity such as imidazole molecules or O^{2-} anions (12):

$$H^{+} + (ImH) \rightarrow (ImH)^{+} \qquad [4]$$

$$H^{+} + O^{2-} \rightarrow OH^{-}. \qquad [5]$$

TABLE 2
Electronic Distribution of the Cations of the Active Oxides

Cu^+	$3d^{10}\,4s^0$
Zn^{2+}	$3d^{10}\,4s^0$
Ga^{3+}	$3d^{10}\,4s^0$
Ag^+	$4d^{10}\,5s^0$
Cd^{2+}	$4d^{10}\,5s^0$
In^{3+}	$4d^{10}\,5s^0$
Hg^{2+}	$5d^{10}\,6s^0$

However, if the ability of the cation to complex basic N is the predominant influence, it is hard to understand the inert behavior of Cu^{2+}, Ni^{2+}, and Co^{2+}, which are also strong amine complexing cations.

The active oxides have a common electronic state of the cation: $nd^{10}\,(n+1)s^0\,(n+1)p^0$ (see Table 2). This configuration is much more polarizable than those of the noble gases ns^2np^6. Furthermore, it has the empty low lying energy levels $(n+1)s$ and $(n+1)p$, which can receive the nonbonding electron pair of N3 in a suitable oriented $(n+1)sp^x$ hybrid orbital. They also have the possibility of π back donation of the d^{10} electrons to vacant aromatic orbitals of the imidazole anion. All these features might be relevant in the reactivity of these oxides.

CONCLUSIONS

The soft imidazole crystals can react with ZnO by hand milling, disrupting the strong cohesive forces of the oxide with a melting point of 1975°C in a few minutes. The reaction also proceeds with Cu^{1+}, Ag^{1+}, and Hg^{2+} with high velocities. Cd^{2+}, Ga^{3+}, and In^{3+} oxides react slowly on strong mechanical milling. The reaction products are the insoluble imidazolates. All the reactive oxides have the cation electronic structure nd^{10}, $(n+1)s^0$, $(n+1)p^0$. Very basic oxides such as Mg^{2+}, Ca^{2+}, Ba^{3+}, and Al^{3+} are inert. The reaction mechanism involves complexing of the cation with the basic N3 atom and formation of a complex which leads to ionization of N1–H.

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