Phase Transitions in Solid Hydrogen-bonded p-Chlorobenzamide, p-Nitrophenol & an Azo Dye†

SOMANATH GANGULY* & GAUTAM R. DESRAJU
Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012

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Phase transition of p-chlorobenzamide, p-nitrophenol and an azo dye, 2-amino-3-hydroxy-6-phenylazoypyridine have been characterized by differential scanning calorimetry, infrared spectroscopy and X-ray crystallography.

The study of phase transitions in solids is of topical interest. However, not much effort has been directed towards the study of transitions in organic solids1. Rao and coworkers studied the phase transitions in dichlorobenzene2 and malonic acid3. In malonic acid4 a transition at 360K where the transition form I and II transforms into III at 393K is characterised by differential scanning calorimetry, infrared spectroscopy and X-ray crystallography.

In BA, the conformation is defined by the angles of the phenyl rings with respect to the plane defined by the four atoms viz. C(1), C(H), N and C(1) which form a bridge between them. Similar conformational polymorphism is expected in AHP since the central bridge in AHP is isoelectronic with that in BA.

Theoretical estimates9 of the energy difference between the conformational polymorphs of BA are about 4 kJ mol⁻¹. The enthalpies of transitions amongst the polymorphs of AHP are also around this value. It is, therefore, possible that at least some of these transitions arise from conformational changes, i.e. the transitions involving changes in the torsion angles about the plane defined by the central atoms C-6, N-1, N-2, and C-1. This is so because a particular pair of torsion angles characterises a particular polymorph. Another possibility for phase transitions in AHP may arise due to a change amongst the tautomeric forms of AHP. For example, AHP could exist as a hydrazone in phase-I and transform into the azopyridinol form at higher temperatures. Conformational polymorphism could also be defined for the hydrazone structure as rotations of the phenyl rings about the C-N or N-N single bonds with respect to the pyridone ring.

In the case of p-chlorobenzamide, three forms, α, γ, and δ, have been recently reported based on X-ray studies10. The α form (P1) undergoes a reversible solid state transition to (P1). Our DSC studies have shown that the α-γ transition occurs at 313K with ΔH of 0.88kJ mol⁻¹. The small magnitude of ΔH agrees favourably with the slight molecular reorientation and co-operative displacements found in X-ray studies. It is interesting that the IR spectra of the two forms are slightly different in the carbonyl region; α-phase νCO at 1705 cm⁻¹ disappears above the α-γ transition. In addition, bands at 1180 and 1785 cm⁻¹ appear as doublets in the α-phase.

A second irreversible transition (γ-δ) has been observed at 400K (ΔH=0.023kJ mol⁻¹), but judging from the very small value of ΔH it would be speculative to comment on the nature of the structural changes involved here.

DSC measurements on p-nitrophenol show a transi-
tion from the metastable $\beta$-form ($P2_1_3$) to the stable $\alpha$-form ($P2_1_2_1_1\alpha$) at 304K ($\Delta H = 0.6$ kJ mol$^{-1}$). This phase transition was first reported by Cohen et al.\textsuperscript{11} who observed it to occur at 323K or near about. The very small value of $\Delta H$ found in this study is consistent with the great similarity between the structures of the $\alpha$- and $\beta$-forms\textsuperscript{12}. The difference in stability of the two forms was expressed in terms of different coordination numbers ($\alpha$, 13 and $\beta$, 10) of the two structures. This is reflected in small transition enthalpy for $\beta\rightarrow\alpha$ transition. Our IR study of the two forms shows that $\nu$OH is slightly broader in the higher temperature phase (at 3340 cm$^{-1}$) than in the low temperature phase (3360 cm$^{-1}$).

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References


Preparation of Copper Zirconate by Thermal Decomposition of Copper Zirconyl Oxalate

V. B. Reddy, C. R. M. Rao & P. N. Mehortra*
Department of Chemistry, University of Roorkee.
Roorkee 247 672

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Copper zirconyl oxide tetrahydrate (CuZrOx) is prepared and its thermal decomposition investigated employing TG, DTG and DTA techniques. The decomposition proceeds through three steps: (i) dehydration between 30° and 145° C, (ii) decomposition of the oxalate between 145° and 400° C and (iii) decomposition of intermediate non-stoichiometric carbonate to give a mixed oxide, CuZrO$_2$. On the basis of the results obtained, a tentative scheme for the decomposition of CuZrOx has been proposed. The X-ray diffraction studies of the end product (CuZrO$_2$) indicate that it belongs to orthorhombic crystal system with $a=6.446\AA$; $b=7.400\AA$; $c=8.312\AA$.

Preparation of mixed oxides by various methods has been of recent interest, since the mode of preparation of a particular solid considerably affects its properties. In recent times some simpler methods have been developed\textsuperscript{24-26} for the preparation of various mixed oxides. Zirconium is known to form anionic oxalatozirconates of bivalent metal cations\textsuperscript{26}, but there is no information available regarding the oxalatozirconate of copper. Hence, the preparation and thermal decomposition of copper zirconyl oxide tetrahydrate (CuZrOx) has been undertaken. A tentative scheme for the decomposition of copper-zirconyl oxide has been proposed. Various stages are characterized by thermogravimetric and isothermal studies, chemical analysis, IR data and X-ray analysis.

All the reagents used were either of BDH(AR) or E. Merck (proanalysis) grade. Zirconium oxychloride octahydrate(Fluka AG) was recrystallised twice before use and characterised by its IR spectrum. Copper zirconyl oxide tetrahydrate was prepared by the procedure described elsewhere\textsuperscript{27} using CuCl$_2$, H$_2$O in place of barium chloride. The product was washed with 1% oxalic acid solution and then with acetone and air dried. The yield was only 50 to 60% which may be due to the solubility of the product in acidic medium. The wet chemical analysis of such a sample gave the following data: Found : H$_2$O, 18.0; CuO, 42.3; Cu, 15.8; ZrO, 24.2. Calculated for CuZrO (Cu$_2$O$_2$)$_4$4H$_2$O: are H$_2$O, 17.20; CuO, 42.02; Cu, 15.18; ZrO, 25.60%. The procedures for physical studies such as TG, DTG, DTA and IR were the same as described earlier\textsuperscript{19}. The $\alpha$-alumina was used as reference in DTA where heating rate was 10°C/min. The heating rate used in TG was 7°C/min. The X-ray powder patterns of the end product were taken on Philips diffractometer using CuK$\alpha$ radiation.

Figure 1 shows the DTA, TG and DTG curves of CuZrOx. From the TG and DTA curves it is evident that all the changes are accompanied by mass loss as one to one correlation exists between DTG and DTA curves. The decomposition of CuZrOx occurs mainly in three steps: (i) dehydration, (ii) decomposition of the oxalate and (iii) decomposition of the non-stoichiometric intermediate compound to give a mixed oxide. TG analysis indicates that the acetone washed sample of CuZrOx loses about 2.5 mols of water between 30° and 150° C giving another hydrate. The peak temperatures for this thermal change are 120° and 100° C on DTA and DTG respectively. The percentage mass loss is 11.10 against the calculated value of 11.20. The remaining 1.5 mols of water are lost along with the decomposition of oxalate, which may indicate that this water is differently bonded in CuZrOx.

Decomposition of oxalate is observed between 145° and 400° C in TG and as an endothermic peak at 310° C in DTA followed by an exothermic peak around 420° C. The latter may probably be due to the oxidation of carbon monoxide and/or oxidation of carbon produced during the disproportionation of carbon monoxide. The mass loss in TG indicates that remaining 1.5 mol of water are also lost along with the oxalate decomposition and a non-stoichiometric residue is obtained. The observed mass loss