New Phase Transition at 155 K and Thermal Stability in KHCO₃

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The differential scanning calorimetry and thermogravimetry of KHCO₃ indicate new transformation anomalies at 155 K (T_{c2}), 373 K (T_d) and 459 K. The former anomaly is likely to be caused by a structural phase transition, but the latter two anomalies are related to the thermal decomposition. The chemical reaction begins at about 373 K (T_d) and reaches a complete thermal decomposition of KHCO₃ into K₂CO₃ around 459 K. The experimental results are discussed in terms of protonic intrabond and interbond jump.

KEYWORDS: KHCO₃, phase transition, thermal decomposition, protonic defects

§1. Introduction

The crystal of KHCO₃ is composed of K⁺-ions and $(HCO_3^{-})_2$ -dimers in which CO_3 groups are bonded by a double hydrogen bond. There is no hydrogen-bonded network through a crystal so that KHCO₃ crystal is classified in the zero-dimensional hydrogen-bonded crystal. The KHCO₃ crystal undergoes a structural phase transition at 318 K (T_{c1}) .^{1–13)} The phase transition involves a symmetry change from the monoclinic phase I (space group $C2/m-C_{2h}^3$) to another monoclinic phase II (space group $P2_1/a-C_{2h}^5$) and is driven by the orderdisorder process of the $(HCO_3)_2$ dimers.³⁾ The protons within the $(HCO_3)_2$ -dimer are in disordered state with two equilibrium positions separated along the hydrogen bond direction.^{4,5} Anomalous elastic behavior in the vicinity of 318 K (T_{c1}) indicated that the I–II transition is of ferroelastic,²⁾ but Brillouin scattering experiments by Takasaka *et al.*⁶⁻⁹⁾ showed that the softening of</sup>transverse acoustic modes is not complete and that KHCO₃ undergoes an antiferrodistortive phase transition of the order-disorder type. The ferrodistortive phase transition to the phase III (true ferroelastic phase, triclinic) occurs by an appropriate external stress both in the phase I and in the phase II. Ferroelastic domains that belong to the triclinic system are sometimes observed in the phase II, indicating phase coexistence of monoclinic phase II and triclinic phase III at room temperature.¹⁰⁾ By the measurements of the dielectric constant, thermal analysis, X-ray diffraction and electrical conductivity, Abdel-Kader *et al.*¹¹⁾ suggested a new phase transformation around 365 K and Ali et $al.^{12,13)}$ reported anomaly near 240 K. But the experimental results for new phase transformations are so poor that the nature except a structural phase transition at 318 K (T_{c1}) is not yet clarified. In this work, we carried out thermal study in order to search for new phase transitions of KHCO₃ and throw some light on the nature of the transformations.

§2. Experimental

The crystals of KHCO₃ were finely crushed into powders for differential scanning calorimetry (DSC) and thermogravimetry (TG) and dried at 353 K for two days for removal of water molecules adsorbed at the surface of each grain. This sample preparation is important for reproducible experimental results. DSC and TG were performed using differential scanning calorimeter (DSC 2010) and TA Instruments (TGA 2050) thermal analyzer system, respectively. Measurements were carried out in the heating process with heating rates of 5 Kmin⁻¹ for DSC and 2 Kmin⁻¹ for TG in a nitrogen atmosphere.

§3. Results

Figures 1, 2 and 3 show a DSC scan of KHCO₃ contained in an aluminum pan in a nitrogen atmosphere. The I–II phase transition was confirmed as an endothermic peak at 317.4 K (T_{c1}). In addition, new transformation anomalies were endothermically detected as a small peak at 155 K, a broad shoulder between 373 and 413 K and a large peak at 459 K. The small endothermic peak at 155 K suggests a new structural phase transition, so we designate 155 K as T_{c2} and the low-temperature phase below T_{c2} is labeled as the phase IV. The onset and



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Fig. 2. DSC scans of $KHCO_3$ with enlargements of DSC signals, revealing phase transitions.



Fig. 3. DSC scans of $KHCO_3$ with enlargements of DSC signals, revealing onset of thermal decomposition.

offset temperatures of broad shoulder were detected at 373 and 413 K, respectively. The large endothermic peak at 459 K means a drastic change of crystal. The following thermogravimetry will give hints whether or not the high-temperature transformations are the structural phase transitions or chemical reactions.

Figure 4 shows a thermogram of KHCO₃ contained in a platinum pan. The mass loss takes place in two stages. The first mass loss begins in the vicinity of 373 K and reaches a loss of 16.0% at 441 K (inflection point in the thermogram). The second decomposition stage accompanied by mass loss more than 16.0% starts about 441 K. Above 441 K, thermal decomposition is in deceleratory stage and the residue of final products reaches a value of 69.0% at 465 K. Of course, different experimental conditions such as environmental atmosphere, heating rate, particle size, defect concentration in the crystal and etc. can also affect the thermal properties of KHCO₃. In fact, the onset temperature of mass loss strongly varied from 368 to 383 K from sample to sample.

Hisatsune and Adl^{1} have studied the thermal decomposition reactions of KHCO₃ dispersed in the KBr pressed disk by observing the changes in the infrared spectrum of the disk with heating. They interpreted the thermal decomposition of KHCO₃ in terms of the following sequence of reactions:



Fig. 4. TG of KHCO₃.

$$(\text{KHCO}_3)_2(s) \rightarrow 2\text{KHCO}_3(s)$$
 (1)

$$2\text{KHCO}_3(s) \rightarrow 2\text{KHCO}_2(s) + \text{O}_2(g) \tag{2}$$

$$2\mathrm{KHCO}_3(s) \rightarrow \mathrm{K}_2\mathrm{CO}_3(s) + \mathrm{H}_2\mathrm{O}(g) + \mathrm{CO}_2(g) (3)$$

where the letter s or g enclosed in parentheses denote that the corresponding compound is in the solid state or gas state. Reaction (1) means a transformation of the bicarbonate dimer into two monomer ions. Continued heating causes the monomer ion to decompose like reactions (2) and (3). The temperature range of each reaction was reported to be 413–493, 693–773, and 723– 823 K, respectively.¹⁾

The present experimental results are interpreted on the basis of above equations. But there were big difference between Hisatsune and Adl¹⁾ and ours about reactions and transformation temperatures. The first mass loss begins in the vicinity of 373 K and reaches a loss of 16.0% at 441 K (inflection point in the thermogram). This is consistent with the theoretical mass of 84.0% for the formation of KHCO₂ according to the eq. (2), that is to say, the removal of one O_2 molecule per molecule of the starting material KHCO₃ dimer. According to eq. (1), we can expect the reaction of the cyclic bicarbonate dimer into two monomeric anions. This is of course possible if the hydrogen bonds are broken and suggest a new structural phase transition without accompanying mass loss. But DSC did not show an anomaly corresponding to monomerization due to hydrogen-bond breaking below the onset of thermal decomposition at 373 K (T_d) . Therefore it may be reasonable that in the case of the thermal decomposition reactions of $KHCO_3$ chemical reactions of eq. (1) and eq. (2) occur competitively and simultaneously. The present thermal analysis shows that the existence of a phase transformation around 365 K^{11} is negative.

The second decomposition stage accompanied by mass loss more than 16.0% starts about 441 K. Above 441 K, thermal decomposition is in a new stage and the residue of final products reaches a value of 69.0% in good agreement of eq. (3) accompanied by the escapes of H₂O gas and CO₂ gas and complete thermal decomposition of KHCO₃ into K₂CO₃.

(4)

§4. Discussions

KHCO₃ is a proton conductor¹⁴⁾ so that the nature of the anomalies at 155 K (T_{c2}) and 373 K (T_d) is likely to be related to the proton motions. The transition 155 K (T_{c2}) may be due to the freezing of proton tunneling motion or freezing of reorientational motion of carbonate ions and the transformation at 373 K (T_d) originates from the proton hopping and breaking of hydrogen bonds. So we should consider what kind of proton defects can be excited in KHCO₃.

In the crystal family of KH_2PO_4 ,^{15,16)} proton intrabond and interbond transfer in $O-H \cdots O$ bonds is the mechanism for dynamic behavior of ferroelectricity and electrical conductivity. Because of strong proton-proton interaction, such transfer is associated with thermally activated creation of H_3PO_4 and HPO_4 intrinsic "Takagi" defects (ionization defects), their hindered diffusion in a random-step fractal potential, and their eventual annihilation. The orientational defects, D (two hydrogens within the $O \cdots O$ bond) or L (lack of hydrogen), are proposed. They are thermally formed in pairs by interbond jumping between different $O-H \cdots O$ bonds, but migrate individually. Proton conduction seems to be related to the presence of defects such as the H_3PO_4 and HPO_4 ionization defects and/or D or L defects.

There is an another kind of defects introduced recently by Lee.¹⁷⁾ On heating MH₂RO₄-type (M=K, Rb, Cs, Tl; R=P, As) crystals, high-temperature phase transition (HTPT) has been known to occur around the onset temperature T_p . Lee claimed that the term HTPT around T_p in MH₂RO₄-type crystals should be replaced by that onset of partial polymerization at reaction sites at the surface of solids,¹⁷⁾ i.e., according to reaction:

$$n\operatorname{MH}_2\operatorname{RO}_4(s) \to \operatorname{M}_n\operatorname{H}_2\operatorname{R}_n\operatorname{O}_{3n+1}(s) + (n-1)\operatorname{H}_2\operatorname{O}(g),$$

that is,



where the letter s or g enclosed in parentheses again denote that the corresponding compound is in the solid state or gas state. Therefore, the intrabond and interbond jumps may be dominant on approaching T_P of thermal decomposition of KH₂PO₄ crystal at the surface and new kind defects of polymeric ions can be generated due to hydrogen-bond breaking. The onset temperature T_P of high-temperature transformation in

hydrogen-bonded crystals has been found to vary over the wide range being strongly dependent on the source of the specimen,^{17–23)} the reason of which may be due to the different distribution of defects at the surface from crystal to crystal. It reveals indirectly the inherent tendency of thermal decomposition of crystal accompanied by dehydration at the surface and the topochemical nature^{24–26)} of the high-temperature phenomenon around T_P .

The very similar consideration can be extended to the case of proton transfer in $\rm KHCO_3$. The protons migrate and change their equilibrium positions in double minimum potential well in various ways, for example, in Fig. 5.

As shown in Fig. 5(a), it is possible for two protons to tunnel or hop in a concerted way, $O-H \cdots O \rightarrow O \cdots H-O$ along the same bond within the dimer. The eightmembered hydrogen-bonded ring can perform a 180° flip about the $C \cdots C$ vector and generate similar protonic configuration, but from one bond to other bond as shown in Fig. 5(b). A proton may jump from one position to the other along the same bond. This type is an intrabond jump in which proton transfers from one bicarbonate group to another, giving rise to "ionization" defects H_2CO_3 and CO_3^{2-} . It is also possible for protons to jump from one bond to another on the same bicarbonate group (interbond jump), giving rise to "orientational" defects: L and D defects. Such an interbond jump leaves a hydrogen bond without a proton (L defects) and produces a bond with protons in each of its two proton positions (D defects). Therefore, protons can migrate through the hydrogen-bonded network by concerted two-proton jumps, intrabond and interbond jumps.

The high-temperature anomaly of KHCO₃ observed about 373 K (T_d) may be understood as due to partial thermal decomposition at reaction sites at or near the surface of crystal, rather than a structural phase transition. The preliminary optical observation supports this interpretation and spatio-temporal pattern will be



Fig. 5. Two possible mechanisms of two proton transfer within the dimer in KHCO₃. (a) tunneling or jumping in a concerted way along the same bond within the dimer. (b) a 180° flip about the C···C vector from one bond to other bond.

reported separately. Although both MH₂RO₄-type crystals and KHCO₃ undergo thermal decomposition at high temperatures, there is a big difference between MH₂RO₄type crystals and KHCO₃. In MH₂RO₄-type crystals, monomers condenses into polymers according to reaction (4) and so the onset temperature is designated as T_p . On the other hand, in KHCO₃ dimers are decomposed into monomers via intermediate stage of reaction (1) and so onset temperature is designated as T_d .

In the higher temperature region we should involve the formation of protonic defect HCO_3 molecules on lattice cation sites by proton transfer from HCO_3 ions to another carbonate molecules, because the migration of protonic defects requires low energy in the lower temperature region and so defect formation requires most of energy, assuming that the HCO_3 ions in $KHCO_3$ is in a state of torsional oscillation, from which it changes to a state of free rotation in the vicinity of 373 K. This free rotation might cause the generation of a large number of protonic defects giving rise to an increase in electrical conductivity. In order to test which kinds of defects contribute to the electrical conductivity, the detailed experimental study is underway and will be reported elsewhere.

§5. Conclusions

We found the new transformation anomalies at 155 K $\,$ (T_{c2}) , 373 K (T_d) and 459 K in KHCO₃. The lowtemperature transformation is likely to be due to freezing of proton motions, while the high-temperature transformation begins at temperature 373 K (T_d) well below 459 K. The bulk mass of $KHCO_3$ decreases at temperature 373 K (T_d) which is interpreted as an onset of partial thermal decomposition, i.e., the chemical reaction begins at about 373 K (T_d) and reaches a complete thermal decomposition of KHCO₃ into K₂CO₃ around 459 K. The first stage of two high-temperature transformations is accompanied by the escape of O_2 , and the second stage is related with the loss of H_2O and CO_2 . These phenomena are discussed in terms of proton migration through the hydrogen-bonded network by concerted two-proton jumps, intrabond and interbond jumps.

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