Thermochimica Acta 532 (2012) 183–186

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Order–disorder phase transition in crystalline di-*tert*-butylphosphinic acid dimer: The role of the ice rules and quantum tunneling

Kouhei Ueda*, Masaharu Oguni

Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku,Tokyo 152-8551, Japan

ARTICLE INFO

Article history:
Available online 21 December 2010

Keywords:
Hydrogen bond
Order–disorder phase transition
Proton tunneling
Heat capacity
Calorimetry

ABSTRACT

Heat capacities of di-*tert*-butylphosphinic acid (abbreviated as DTPA) crystal were measured by adiabatic calorimetry. Phase transition of a second-order type was discovered at 37.8 K. The entropy of the transition was estimated to be 2.6 $J K^{-1} mol^{-1}$, and the magnitude was interpreted as suggesting that the transition is attributed to the order–disorder process of the hydrogen-bonded protons of a DTPA dimer and that the protons rearrange with always keeping the ice rules. It was discussed that the real state of the protons should be described on the consideration of the tunneling between the two configurations which are represented classically as each proton is located close to either of the two oxygen atoms forming a hydrogen bond.

1. Introduction

Hydrogen bond such as O–H···O is one of the most important inter-molecular interactions. For example, among the substances with almost the same molecular sizes, the gas–liquid critical temperatures of the substances with hydrogen-bond-forming hydroxyl or amine groups are remarkably higher than those of the ones without the groups. This indicates that the bonds produce strong attractive force between the molecules. The detail of the hydrogen-bond network in the crystalline state is thus expected to affect strongly the properties of substances.

Proton is, meanwhile, lightest in the mass among nuclei. The lightness causes the proton to show an appearance of interesting quantum effect; tunneling between two sites in the bond with a short O···O length around 2.5 Å. The presence of such effect has been long discussed in potassium dihydrogen phosphate (KDP) with a three-dimensional hydrogen-bond network [1]: The crystal in reality displays a phase transition at 120 K to bring an ordered arrangement of the protons at lower temperatures. The transition temperature increases to 230 K by deuterium substitution; the increase of c.a. 100 K by the substitution is too large as compared with that, about 5 K, found in the transition temperatures of the proton ordering in the cases with O···O length around 2.7–2.8 Å. The large increase has been believed as originating from the tunneling potentially occurring [2]. In 5-bromo-9-hydroxyphenalenone, the evidence of the tunneling occurring was really reported [3,4]: No transition was observed to a low-temperature phase, a Schottky anomaly due to the splitting between the ground and excited tunneling states of the proton was detected by calorimetry, and the splitting was directly observed by infra-red spectroscopy [5,6]. In this crystal, a hydrogen bond is formed within each molecule and isolated from other hydrogen bonds without its extended network. In crystals of dimeric carboxylic-acid derivatives, the presence of a similar tunneling effect has been reported by using NMR methods [7,8]. However, no Schottky anomaly nor tunneling-energy splitting have been detected by calorimetry or spectroscopy.

Crystalline phosphinic acid (R_2POOH) generally forms short and strong hydrogen bonds. The structural character is that one-dimensional chain or cyclic-dimer network structures are formed with the hydrogen bonds. For example, dimethylphosphinic acid forms a chain structure [9], and dicyclohexylphosphinic acid a cyclic-dimer one [10]. Hydrogen-bond network structure and the character of the hydrogen bonds are of course influenced by the properties of R-groups; namely, their size, symmetry, electronegativity, and so on. As these network structures are in between the above two of three-dimensional and isolated ones and similar to the carboxylic acid derivatives, the behaviors of the hydrogen-bonded protons in these systems are attractive to be clarified. The crystal structure of di-*tert*-butylphosphinic acid (abbreviated hereafter by DTPA) was already determined at room temperature by Druyan et al. [11]: Two DTPA molecules form a cyclic dimer with two hydrogen bonds. The two hydrogen bonds have two remarkable features with respect to bond lengths. One is that the lengths of the two P–O bonds in each DTPA molecule are about 1.52 Å and essentially the same within the experimental error; however, the two P–O bonds are not related by the space group symmetry. The other is that the O···O lengths of the two bonds are ca. 2.5 Å and very short. The first feature indicates that the proton is disordered

* Corresponding author. Tel.: +81 3 5734 2221; fax: +81 3 5734 2222.
E-mail address: kueda@chem.titech.ac.jp (K. Ueda).

0040-6031/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2010.12.008

at two sites close to either of two oxygen atoms in the O···O hydrogen bond at room temperature. In most of other carboxylic and phosphinic acids with a cyclic-dimer structure [2,12], the C–O or P–O lengths are different between the two in a molecule; one is close to a single bond and the other to a double bond. In these cases, the hydrogen-bonded protons have been really found to be located at the positions close to one oxygen atom with C–O or P–O single bond. The second feature interests us with a possibility that quantum tunneling of the proton is operative in the disordering. Cyclic-dimer structure present in DTPA crystal is simplest among the hydrogen-bond networks and provides one of the ideal systems for studying any effect of difference in the network structures on the appearance of quantum tunneling in short hydrogen-bonds.

In this paper, we measured low-temperature heat capacities of the DTPA crystal by adiabatic calorimetry to examine the low-temperature thermodynamic behavior of the hydrogen atoms in the hydrogen bonds. One possibility is that a phase transition takes place as a cooperative positional ordering of protons, and the other is that there appears a kind of Schottky anomaly without the transition. Attention was also paid to the dynamics concerning the proton transfer between the two sites. If enthalpy-relaxation or glass-transition phenomena were observed on the way of the positional ordering or if not, the information should provide valuable knowledge about the rate of proton transfer between the two sites.

2. Experiment

2.1. Sample

DTPA was synthesized according to the procedure described in a literature [13], and purified by the re-crystallization from *n*-heptane, resulting in small colorless crystals. The crystals obtained were confirmed by proton nuclear magnetic resonance (^{1}H-NMR($CDCl_3$)) and powder X-ray diffraction methods to be the desired.

2.2. Calorimetric measurements

The DTPA sample obtained was loaded into a calorimeter cell and the cell was sealed tightly under an atmosphere of helium gas. The mass of the sample used was weighed to be 3.613 g. Heat capacities were measured in a temperature range of 3–300 K with an adiabatic calorimeter by using an intermittent heating method [14,15]. In view of the large sample mass used in the calibration of the calorimeter [15], the inaccuracy and imprecision of the heat capacity data derived presently are expected to be ±1.5% and ±0.3%, respectively.

3. Results and discussion

3.1. Heat capacities and the properties of a phase transition at 37.8 K

Fig. 1 shows the obtained molar heat capacities of DTPA crystal. An anomaly judged as a phase transition was observed with a peak at 37.8 K, as shown in Fig. 2 on an enlarged scale below 80 K. Solid line represents a baseline drawn so as to estimate the anomalous heat capacities due to the phase transition. The line was derived as follows. Heat capacity C_V at constant volume was assumed as expressed by a following Eq. (1):

$$C_v = \sum C_E + \sum C_D, \quad (1)$$

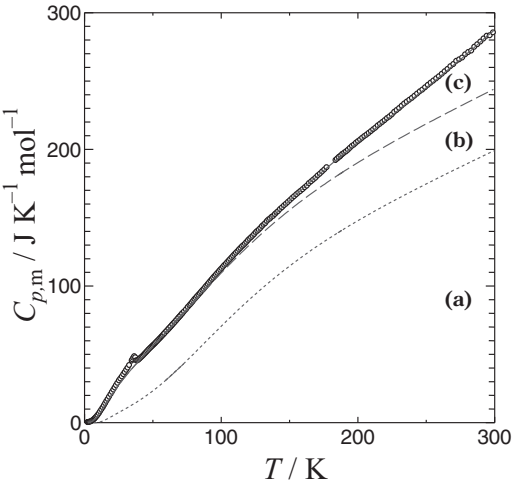

Fig. 1. Heat capacities of DTPA: open circle, experimental data; (a), contribution from 84 degrees of freedom of intra-molecular vibrations; (b), contribution from 6 degrees of freedom of inter-molecular vibrations; (c), $(C_p - C_v)$ term. Solid line represents the sum of the three (a)–(c) as the base line for the anomalous part of heat capacities due to a phase transition.

where C_E and C_D stand for Einstein's and Debye's terms written by the following Eqs. (2) and (3), respectively.

$$C_E = R\left(\frac{\theta_E}{T}\right)^2 \frac{2\exp(\theta_E/T)}{(\exp(\theta_E/T)-1)^2} \quad (2)$$

and

$$C_D = R\left(\frac{T}{\theta_D}\right)^3 \int_o^{\theta_D/T} x^4 e^x (e^x - 1)^{-2} dx, \quad (3)$$

where θ_E and θ_D are Einstein's and Debye's temperatures, respectively. Since DTPA is a molecular compound, the degrees of freedom of intra-molecular vibrations were recognized as well separated from the inter-molecular ones, and their contributions as well expressed by the Einstein's equation. One DTPA molecule has 90 degrees of freedom of normal-mode motions. Among them, 84 degrees of freedom are classified as the intra-molecular normal vibrations, and their frequencies were evaluated according to the computation procedure given by Gamess [16] with the Hartree–Fock method. The sum of the contributions to heat capac-

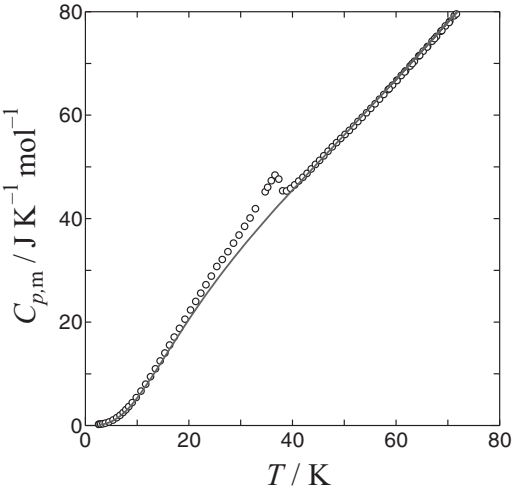

Fig. 2. Heat capacities of DTPA on an enlarged scale below 80 K: open circle, experimental data; solid line, the base line for the anomalous part of heat capacities due to a phase transition.