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OH Bending Vibrations and Hydrogen Bond in Crystalline *p*-Hydroxybenzaldehyde

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The energy of hydrogen bond formed in the crystalline state of *p*-hydroxybenzaldehyde was estimated to be 7.3 kcal/mol from the heat of sublimation.[1] However, it has not yet been determined whether the molecules form a hydrogen bond of the type OH···OH or OH···O=C in the crystal.

Recently we carried out IR measurement in relation to our study on dielectric behavior and three-dimensional X-ray crystal structure analysis of this substance. This note reports on the bending vibrations of OH bond and their temperature variation in the crystalline state of *p*-hydroxybezaldehyde with reference to estimating the strength of hydrogen bond spectroscopically.

p-Hydoxybenzaldehyde was purified by vacuum sublimation and used as a KBr disc for the IR measurement. An IR spectrometer of JASCO IR-S type covering a frequency range 650—4000 cm^{-1} was used. Spectra obtained at several temperatures are shown in Fig. 1.

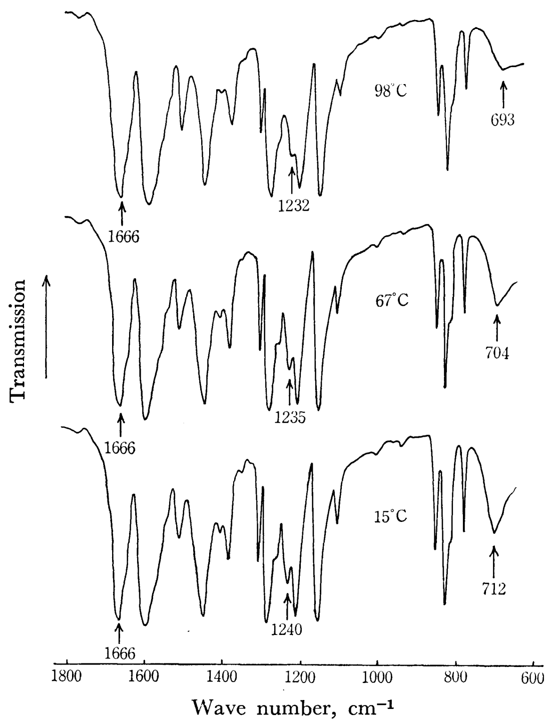

Fig. 1. IR spectra of *p*-hydroxybenzaldehyde (KBr disc) at three temperatures; spectra in the frequeney range, 600—1800 cm^{-1}, are shown.

We note a characteristic feature of a broad band at 712 cm^{-1} (15°C) which shifts towards low frequency side with an increasing breadth with the rise of temperature. Similarly a band at 1240 cm^{-1} shifts slightly in the same direction with a tendency of broadening. On the other hand, the temperature variation of a strong and very broad band at 3180 cm^{-1}, which can be identified to be the OH stretching vibration (hydrogen-bonded), is not clear because of the poor resolving power of the instrument in this frequency region. From the characteristic behavior of these bands, it is almost certain that the 712 cm^{-1} band can be ascribed to the out-of-plane bending vibration of the OH bond intermolecularly hydrogen-bonded to neighboring molecules, and that the 1240 cm^{-1} band is due to the in-plane OH bending vibration under the influence of hydrogen bonding.[2-5]

So far several authors have reported on IR as well

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3) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco (1960), p. 70.

4) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, Inc., New York (1968), p. 85.

as far-IR absorption of *p*-hydroxybenzaldehyde in solution and solid states,[5-8] but none have mentioned the OH bending vibration except for Bellamy[5a] who identified a band at 1160 cm^{-1} as δ_{OH} (in-plane bending vibration).

It is worthy of mention that the frequency of stretching vibration of C=O group 1666 cm^{-1} remains almost the same all through the temperature variation. This suggests that the carbonyl group is not involved in hydrogen bond formation in the crystalline state and the hydrogen bond in the crystal is very likely of the type, OH···OH···OH···.

A similar suggestion has been made by Fukushima[8] from far-infrared measurement.[9]

In order to estimate the energy of hydrogen bond from the frequency shift of OH vibration on hydrogen bonding, an empirical equation proposed recently by Purcell and Drago[10] has been used: $-\Delta H(\pm 0.5$ kcal/mol$)=0.016\times\Delta\nu_{OH}+0.63$, where ΔH is the energy of the hydrogen bond and $\Delta\nu_{OH}$ the frequency shift in cm^{-1}. Since the equation was derived originally for the anharmonic stretching vibration of a bond involved in hydrogen bonding, estimation of ΔH was made first with the frequency shift of OH stretching vibration observed in this experiment. Taking 3594 cm^{-1} observed in CCl_4 solution[11] as the free OH stretching vibration, $\Delta\nu_{OH}=3594-3180=414$ cm^{-1} leads to ΔH value of 7.25 kcal/mol which is in good agreement with the value 7.3 kcal/mol obtained thermochemically.[1]

A tentative calculation of the energy of the hydrogen bond has been made with the use of the frequency shift of the out-of-plane bending vibration 412 cm^{-1}, the difference between $\gamma_{OH}=712$ cm^{-1} observed in this measurement and $\gamma_{OH}=300$ cm^{-1} assigned to the free OH libration in phenol molecules.[12,13] The result obtained is almost the same as mentioned above, *viz*., 7.23 kcal/mol. It is reasonable to infer that the anharmonicity of OH libration is reduced to a greater extent due to hydrogen bonding, making the Purcell and Drago equation applicable to the bending vibration in this case.

In the crystalline state of *p*-hydroxybenzaldehyde, the decrease of energy of the hydrogen bond with the rise of temperature can be estimated by following the above procedure as shown in Table 1.

TABLE 1. TEMPERATURE VARIATION OF OH BENDING VIBRATION AND THE ENERGY OF HYDROGEN BOND IN CRYSTALLINE *p*-HYDROXYBENZALDEHYDE ESTIMATED WITH THE USE OF THE PURCELL AND DRAGO EQUATION

Temp. °C	15	50	67	88	98
γ_{OH} cm^{-1}	712	710	704	697	693
ΔH kcal/mol	7.22	7.19	7.10	6.98	6.91
δ_{OH} cm^{-1}	1240	1238	1235	1233	1232
ΔH kcal/mol	1.85	1.62	1.57	1.54	1.53

The decrease in ΔH as seen in the table might be correlated with the increase of O···O distance with the rise of temperature. The OH in-plane bending vibration would be unsuitable to be correlated with the strength of hydrogen bond[5b]: much smaller values of ΔH were obtained from $\Delta\delta_{OH}$ (Table 1) assuming 1176 cm^{-1} observed with phenol vapor[14] to be the free OH bending frequency.

A hindered rotator model with a potential

$$V = (V_0/2)(1-\cos n\theta)$$

can be applied also to calculate the energy of hydrogen bond, if we assume that V_0 is composed of two parts, *i.e.*, an attractive potential due to hydrogen bonding and a repulsive one which is intrinsic to a molecule free from hydrogen bonding. In the above equation, θ is an angle of rotation and n is the number of equilibrium positions the rotator will occupy during the rotation through 360°. Since the frequency of libration in the potential well can be expressed as

$$\nu = (n/2\pi)(V_0/2I)^{1/2}$$

where I is the moment of inertia of the rotator, we get V_0 by substituting the observed value of out-of-plane bending vibration $\gamma_{OH}=712$ cm^{-1} into the equation with appropriate values of I and n. Putting $n=2$, and assuming that the dimension of OH group in *p*-hydroxybenzaldehyde is the same as that of phenol molecule with $I=1.23\times10^{-40}$ gcm^2 (ref. 14), we obtain $V_0=15.96$ kcal/mol. Therefore, subtracting the hindering potential for the OH rotation in a phenol molecule 3.48 kcal/mol[13] from the V_0 value, we get 12.48 kcal/mol as the energy of hydrogen bond in *p*-hydroxybenzaldehyde crystal. The value is somewhat larger than those estimated with the use of the frequency shift on hydrogen bonding 7.22 kcal/mol, probably because the above equation is applicable only in the vicinity of the potential minimum. Or, we might presume that the hindering potential of the OH group in a free molecule of *p*-hydroxybenzaldehyde should be larger than that of a phenol mloecule, due to the reinforced effect of conjugation of the C–O bond with the benzene ring in the presence of an aldehydic substituent at the *para* position.

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