The Far-infrared Spectra of Some Phenols

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Many greatly-successful infrared investigations of substances with the X–H···Y hydrogen bond have been made using the X–H stretching absorption band. However, it seems that these have not given any information on the minute differences in the conformation of the X–H···Y group.

The infrared absorption band due to a vibration of the X–H···Y group, which is expected to give more information about the conformation of the X–H···Y group, appears in the far-infrared spectral region. Green et al. have found a band in the far-infrared spectra of phenol in the crystalline state; they have tentatively assigned it to the stretching vibration of the O–H···O group.[1] Stanevich has measured the far-infrared spectra of crystalline phenol, *m*- and *p*-nitrophenols, hydroquinone, resorcinol, *o*-nitrophenol, and 2,6-dinitrophenol. He has found that only in the case of phenol does a frequency shift when it is dissolved into a non-polar solvent.[2]

In the present investigation, the far-infrared spectra of *o*- and *p*-hydroxybenzaldehydes and *o*- and *p*-methoxyphenols will be measured and compared with those of carbon tetrachloride solutions.

Experimental

Material Employed.—*o*- and *p*-Hydroxybenzaldehydes and *o*- and *p*-methoxyphenols were of the reagent grade. Phenol was recrystallized from its carbon tetrachloride solution.

Infrared Spectra.—The infrared spectra were recorded with a Perkin-Elmer model 201C far-infrared spectrometer in the region from 80 to 350 cm^{-1}, and with a Perkin-Elmer model 221 spectrophotometer equipped with a LiF prism in the region from 2800 to 3800 cm^{-1}.

The spectra of crystals were measured in Nujol mull sandwiched between two polyethylene plate 1 mm. thick while those of solutions were measured using liquid cells with polyethylene windows 3 mm. thick. The concentrations of the solutions and the cell thicknesses are listed in Table I. The sample solution of phenol in carbon tetrachloride was prepared by the dilution of its saturated solution with carbon tetrachloride in a volume ratio of 1 to 12.5. The spectra obtained are shown in Figs. 1—8.

TABLE I. CONCENTRATION OF SOLUTIONS AND CELL THICKNESS

Substance	Concn.	Cell thickness	
$C_6H_5(OH)$		2	
o-$(CHO)C_6H_4(OH)$	0.38	2	(Fig. 5)
	0.15	5	(Fig. 6)
o-$(CH_3O)C_6H_4(OH)$	0.46	2	(Fig. 8(A))
	0.18	5	(Fig. 8(B))

* Concentration in mol./l.; Cell thickness in mm.

Results and Discussion

As Figs. 1—3 show, it is clear from the frequency values of O–H stretching bands in the 3μ region (phenol, 3279 cm^{-1}; *p*-hydroxybenzaldehyde, 3175 cm^{-1}) that strong hydrogen bonds are formed in phenol and *p*-hydroxybenzaldehyde in the crystalline state. Both these compounds have a band in the region from 170 to 180 cm^{-1} (phenol, 172 cm^{-1}; *p*-hydroxybenzaldehyde, 180 cm^{-1}). The band at 170 cm^{-1} of phenol has been assigned to the stretching vibration of the O–H···O group by Stanevich, on the basis of its frequency change observed through the change in the state from crystal to solution.[1] This frequency

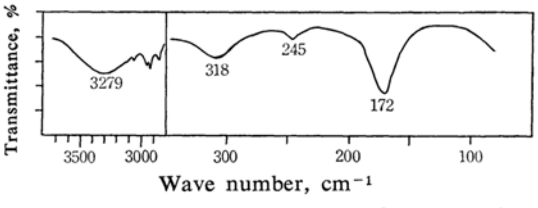

Fig. 1. Far-infrared spectra of phenol in crystalline state.

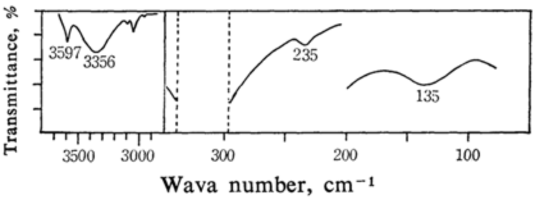

Fig. 2. Far-infrared spectra of phenol in carbon tetrachloride solution.

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[1] J. H. S. Green, W. Kynaston and H. A. Gebbie, *Nature*, **195**, 595 (1962).

[2] A. E. Stanevich, *Optics and Spectroscopy*, **16**, 539 (1964).

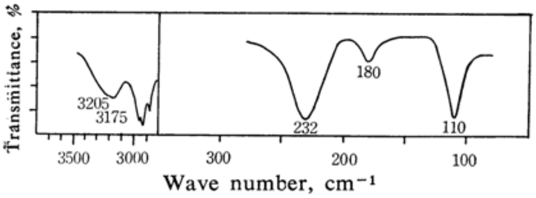

Fig. 3. Far-infrared spectra of *p*-hydroxybenzaldehyde in crystalline state.

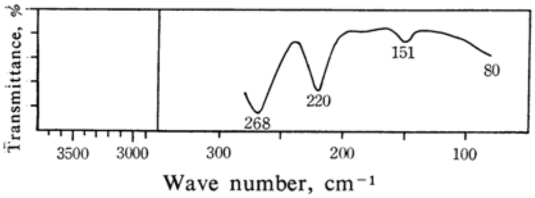

Fig. 4. Far-infrared spectra of *o*-hydroxybenzaldehyde in liquid state.

change was confirmed by the present investigation, as Figs. 1 and 2 show. Among the three bands in the spectra of *p*-hydroxybenzaldehyde (Fig. 3, 80—300 cm^{-1} region), two bands, at 110 cm^{-1} and 232 cm^{-1}, can be assigned to the vibrations of the CHO-C group by a comparison of the spectra with those of benzaldehyde,* no other bands are expected to appear in the region from 100 to 300 cm^{-1} except for the stretching vibration of the O-H···O group. Therefore, the band at 180 cm^{-1} of *p*-hydroxybenzaldehyde is considered to correspond to the stretching vibration of the intermolecular hydrogen bond.

The band at 179 cm^{-1} in the far-infrared spectra of *p*-methoxyphenol in the crystalline state may correspond to the stretching vibration of the intermolecular hydrogen bond.

It may be suggested, from the fact that the frequency values of the stretching vibration of the intermolecular hydrogen bond are nearly the same in phenol, in *p*-hydroxybenzaldehyde and in *p*-methoxyphenol, that the types of the intermolecular hydrogen bond of *p*-hydroxybenzaldehyde and *p*-methoxyphenol are similar to that of the phenol crystal.3)

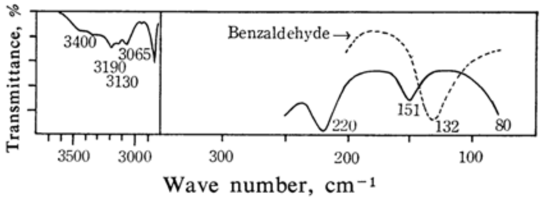

Fig. 5. Far-infrared spectra of *o*-hydroxybenzaldehyde in carbon tetrachloride solution.

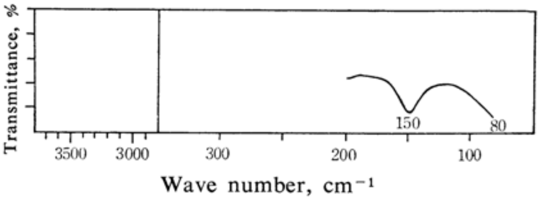

Fig. 6. Far-infrared spectra of *o*-hydroxybenzaldehyde in carbon tetrachloride solution.

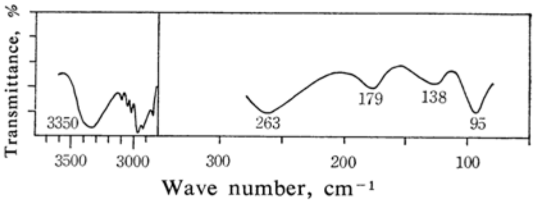

Fig. 7. Far-infrared spectra of *p*-methoxyphenol in crystalline state.

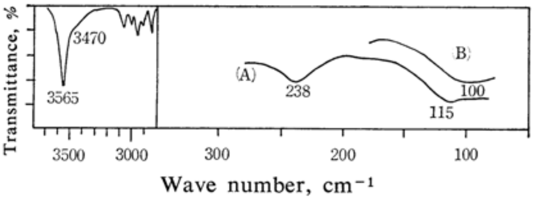

Fig. 8. Far-infrared spectra of *o*-methoxyphenol in carbon tetrachloride solution.

In the case of *o*-hydroxybenzaldehyde in the liquid state, which is considered to have an intramolecular hydrogen bond on the basis of the frequency value of the O-H stretching band in its 3μ region and the geometry of its molecule, no band was observed in the region from 100 to 200 cm^{-1}, except for a band at 151 cm^{-1}. This band can be assigned to a vibration of the CHO-C group by a comparison of the spectra with those of benzaldehyde. When *o*-hydroxybenzaldehyde is diluted with carbon tetrachloride, no change takes place in the spectra, as Figs. 5 and 6 show. Therefore, the bands at 268, 220, 151 and about 80 cm^{-1} in Fig. 4 may reasonably be interpreted as being due to the vibrations of non-associated molecules. As the three bands, 268, 220 and 151 cm^{-1}, can be assigned to the vibrations of the CHO-C group, we might assign the band at about 80 cm^{-1} to the stretching vibration of an intramolecular hydrogen bond. In the spectra of a solution of *o*-methoxyphenol in carbon tetrachloride, the O-H stretching bands were observed at 3565 and 3470 cm^{-1}. The former is due to the O-H stretching vibration of free molecules, while the latter is due to

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* Benzaldehyde has three bands, 130, 224 and 235 cm^{-1}, in the region from 80 to 250 cm^{-1}, these are assigned to the vibrations of the CHO-C group1).

3) C. Scheringer, O. J. Wehrhahn und M. v. Stackelberg, *Z. Elektrochem.*, **64**, 381 (1960).

that of the hydrogen-bonded O-H group. As the intensity of the latter band is very weak, it is expected that the amount of molecules forming a hydrogen bond is not great. Corresponding to this fact, no band that is considered to be due to the stretching vibration of the O-H···O group was observed in the far infrared region, as is shown in Fig. 8.

On the basis of the experimental results in the present investigation, it may be suggested that the frequency value of the stretching vibration of the O-H···O group in the far-infrared region is very sensitive to the structural difference of the O-H···O group and can be useful in the study of molecular structure.

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