# *Intramolecular Interaction between Hydroxyl Group and $\pi$-Electrons. VIII*[1]. *Energetics of the Interaction*

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Little is known of the energy of the intramolecular interation between the hydroxyl group and $\pi$-electrons in spite of many studies on this phenomenon in a number of compounds. In the first paper[2] of the present ·series, the authors reported briefly that the energies of the intramolecular interaction in 2-hydroxy-4- and -4′-nitrobiphenyls are 2.5 and 0.93 kcal./mol., respectively. Goldman and Crisler[3] suggested that the strengths of this kind of interaction in 2-phenylethanol and 2-($p$-methoxyphenyl)-ethanol are 0.88 and 0.98 kcal./mol., respectively, assuming that Badger's postulation, that 70 cm$^{-1}$ shift of the wave number of the hydroxyl stretching bands caused by the hydrogen bond formation corresponds to one kcal./mol. in the energy[4], is operative in this interaction. Necessity of elucidating the true nature of the interaction prompted the authors to examine the energy difference between the free and the interacting forms, since the results would be very useful for the discussion of the relation between band properties and the energy difference and consequently for the discussion of the nature. The present paper deals with some detailed procedures used in the measurement of the energies, which were omitted in the former short communication[2], and reports some data added recently in this laboratory. The materials include 2-allylphenol[1], 2-benzylphenol[1], 2-isopropenylphenol[5] and 2-hydroxybiphenyl[1]. The variation with the temperature of the infrared absorption spectra due to free and interacting hydroxyl groups was measured. These phenols were chosen out of many which possess the internal interaction by considering not only the fundamental structure representing each series, but also some technical advantages. The relative intensities of the free and the interacting O–H stretching absorption bands ($\nu_{O-H}$) at various temperatures can be measured most accurately when the intensities of the two bands are nearly equal. Otherwise, when the most favorable absorbance of one band is secured, the other will be either so weak that it may be affected by the noise of the recording system or so strong that it may exceed saturation. 2-Hydroxybiphenyl does not necessarily fulfill this requirement but the duplicate measurement under the best condition of the spectrometer gave reasonable data, although the probable error was fairly large in this case. To cover all the types of the intramolecular interaction, further combinations of the alcoholic hydroxyl group and the $\pi$-electrons of olefins and aromatic rings must be considered. The alcohol, however, as pointed out previously[6], shows rather complicated $\nu_{O-H}$ consisting

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[1] Part VII: This Bulletin, 33, 681 (1960).

[2] M. Ōki, H. Iwamura and Y. Urushibara, ibid., 31, 770 (1958).

[3] I. M. Goldman and R. O. Crisler, *J. Org. Chem.*, 23, 751 (1958).

[4] R. M. Badger, *J. Chem. Phys.*, 8, 288 (1940).

[5] M. Ōki and H. Iwamura, Presented at the Symposium on the Electronic State of Molecules, Tokyo, Sept. 8, 1959.

[6] M. Ōki and H. Iwamura, 32, 567 (1959).

of two free $\nu_{O-H}$'s of rotational isomers and one interacting $\nu_{O-H}$ and thus obliges some discretion in dividing the apparent curve into absorptions due to free and interacting forms. This phenomenon caused the authors to give up the study of energy in the alcoholic series in the present work.

## Experimental

**Measurement.**—A Perkin Elmer Model 112 G Double Pass High Precision Grating Infrared Spectrometer was used as previous[6], the spectral slit width being 1.0 cm$^{-1}$ in this region. In a quartz absorption cell of 2 cm. length, having a window of 2.5 cm. diameter and protected with a heating coil covered with asbestos, about 20 ml. of the solution of the sample ($c\sim0.001$ mol./l.) in carbon tetrachloride was placed, and the temperature was controlled by varying the current through the heating coil, kept at each equilibrated temperature within $\pm0.2$°C and read by a thermometer dipped in the solution. The spectrometer being of a single beam type, a background trace was recorded every time immediately before the spectral measurement of the solution and the latter was always referred to the former, which also changed a little with the varying temperature.

**Calculation.**—Separation of the apparent curve and calculation of the integrated intensities of the two bands were made according to Ramsay's first method[6,7] for each of the absorption curves at different temperatures.

$$\text{Free form} \rightleftarrows \text{Interacting form}$$

Then the integrated form of the well-known van't Hoff equation (1) can be applied to obtain the energy difference between the two forms.

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{1}$$

$K$ can be given by

$$K = \frac{C_i}{C_f} = \frac{A_i/a_i}{A_f/a_f} = a\frac{A_i}{A_f} \tag{2}$$

where $a_i$ and $a_f$ represent intensities per molecule with a free hydroxyl group and an interacting one, respectively, and $A$'s integrated intensities. Combination of Eq. 1 with Eq. 2 gives

$$\ln\frac{A_i}{A_f} = \frac{-\Delta H}{RT} + \left(\frac{\Delta S}{R} - \ln a\right) \tag{3}$$

The slope of the line obtained by taking $\ln(A_i/A_f)$ on the ordinate and $1/T$ on the abscissa gives the energy of the interaction $(-\Delta H)$. Here it is assumed, that $a_i$ and $a_f$, or at least their ratio $a$, should be independent of the temperature, since the temperature range is rather narrow (25∼70°C).

**Materials.**—Phenols used in the measurements are all known compounds and their physical constants were already reported previously[1,5].

## Results and Discussion

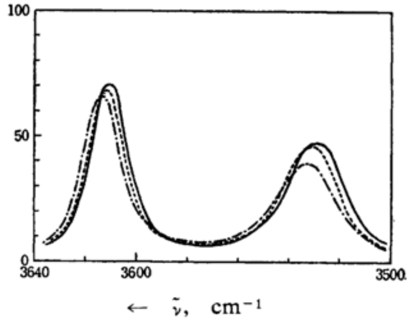

Fig. 1. $\nu_{O-H}$ absorptions of 2-isopropenylphenol at various temperatures.
28.1°C —— 45.3°C ------ 70.5°C -·-·

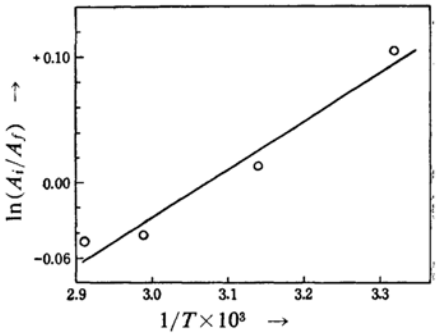

Fig. 2. Relation between $\ln(A_i/A_f)$ and temperature for 2-isopropenylphenol.

Apparent absorption curves of 2-isopropenylphenol at various temperatures are shown in Fig. 1 and $\ln(A_i/A_f)$ and temperature relation in Fig. 2.

The effects of the temperature on the hydroxyl stretching frequencies and on the intensities are summarized in Tables I to IV.

There is always a slight but definite increase in absorption frequencies of both free and interacting $\nu_{O-H}$, accompanied by a decrease in the total integrated intensities $(A_i+A_f)$. These effects might be attributed to the rupture of the remaining hydrogen bonding, but, in concentration employed here ($c\sim0.001$ mol./l.), the possibility of the bonding of two phenol molecules can be neglected with certainty. Liddel and Becker[8] already observed an appreciable decrease in the peak intensity and a slight increase in frequency (ca. 6 cm$^{-1}$) of the free $\nu_{O-H}$ of methanol in carbon tetrachloride in the temperature range between −10 and 50°C, and suggested that these variations might be considered to be owing to a weak hydrogen bonding to the solvent. This possibility is apparently reasonable because this type of interaction may be very weak and the observed shift of the frequencies is only small, besides it can be ruptured easily with the rising temperature. Tables I to IV show, however, that

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[7] D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).

[8] U. Liddel and E. D. Becker, *J. Chem. Phys.*, **25**, 173 (1956).

TABLE I. THE EFFECT OF THE TEMPERATURE ON $\nu_{O-H}$'S OF 2-ALLYLPHENOL

| Temperature $1/T\times10^3$ (°K$^{-1}$) | $\nu_{max}$ (cm$^{-1}$) | $\Delta\nu^a_{1/2}$ (cm$^{-1}$) | $A\times10^{-3}$ (mol$^{-1}$·l.·cm$^{-2}$) | $A_i/A_f$ | $\Delta\nu_{max}$ (cm$^{-1}$) |
|---|---|---|---|---|---|
| 3.31 | 3612.2<br>3547.0 | 17.0<br>62.3 | 6.66<br>8.72 | 1.30 | 65.2 |
| 3.14 | 3613.2<br>3548.6 | 17.4<br>62.8 | 6.58<br>8.55 | 1.30 | 64.6 |
| 3.03 | 3614.1<br>3551.7 | 17.6<br>64.2 | 6.52<br>8.04 | 1.23 | 62.4 |
| 2.92 | 3614.9<br>3556.1 | 18.0<br>65.8 | 6.23<br>7.46 | 1.20 | 58.8 |

TABLE II. THE EFFECT OF THE TEMPERATURE ON $\nu_{O-H}$'S OF 2-BENZYLPHENOL

| Temperature $1/T\times10^3$ (°K$^{-1}$) | $\nu_{max}$ (cm$^{-1}$) | $\Delta\nu^a_{1/2}$ (cm$^{-1}$) | $A\times10^{-3}$ (mol$^{-1}$·l.·cm$^{-2}$) | $A_i/A_f$ | $\Delta\nu_{max}$ (cm$^{-1}$) |
|---|---|---|---|---|---|
| 3.31 | 3611.1<br>3560.6 | 17.2<br>60.8 | 8.48<br>8.67 | 1.02 | 50.5 |
| 3.14 | 3612.0<br>3561.8 | 17.8<br>59.2 | 8.53<br>8.44 | 0.99 | 50.2 |
| 3.04 | 3612.6<br>3565.8 | 17.8<br>60.8 | 8.07<br>7.90 | 0.98 | 46.8 |
| 2.91 | 3613.4<br>3566.9 | 18.4<br>61.8 | 7.90<br>7.55 | 0.96 | 46.5 |

TABLE III. THE EFFECT OF THE TEMPERATURE ON $\nu_{O-H}$'S OF 2-ISOPROPENYLPHENOL

| Temperature $1/T\times10^3$ (°K$^{-1}$) | $\nu_{max}$ (cm$^{-1}$) | $\Delta\nu^a_{1/2}$ (cm$^{-1}$) | $A\times10^{-3}$ (mol$^{-1}$·l.·cm$^{-2}$) | $A_i/A_f$ | $\Delta\nu_{max}$ (cm$^{-1}$) |
|---|---|---|---|---|---|
| 3.32 | 3611.0<br>3529.4 | 16.7<br>26.5 | 4.19<br>4.59 | 1.11 | 81.6 |
| 3.14 | 3612.0<br>3531.9 | 16.8<br>26.0 | 4.08<br>4.28 | 1.01 | 80.1 |
| 2.99 | 3612.8<br>3532.4 | 16.8<br>25.8 | 3.99<br>3.83 | 0.96 | 80.4 |
| 2.91 | 3613.8<br>3533.5 | 17.0<br>25.6 | 3.92<br>3.75 | 0.96 | 80.3 |

TABLE IV. THE EFFECT OF THE TEMPERATURE ON $\nu_{O-H}$'S OF 2-HYDROXYBIPHENYL

| Temperature $1/T\times10^3$ (°K$^{-1}$) | $\nu_{max}$ (cm$^{-1}$) | $\Delta\nu^a_{1/2}$ (cm$^{-1}$) | $A\times10^{-3}$ (mol$^{-1}$·l.·cm$^{-2}$) | $A_i/A_f$ | $\Delta\nu_{max}$ (cm$^{-1}$) |
|---|---|---|---|---|---|
| 3.30 | 3606.9<br>3564.9 | 15.5<br>15.0 | 1.39<br>13.11 | 9.44 | 42.0 |
| 3.19 | 3607.3<br>3565.3 | 15.8<br>15.2 | 1.48<br>12.99 | 8.77 | 42.0 |
| 3.08 | 3607.7<br>3565.9 | 16.0<br>15.2 | 1.63<br>12.57 | 7.72 | 41.8 |
| 3.01 | 3607.9<br>3566.3 | 16.2<br>15.6 | 1.59<br>12.84 | 8.10 | 41.6 |
| 2.90 | 3608.3<br>3566.8 | 17.0<br>15.8 | 1.80<br>12.48 | 6.92 | 41.5 |

TABLE V

| Phenols | $-\Delta H$ (kcal./mol.) | $\Delta S/\boldsymbol{R}-\ln a$ | $\Delta\nu_{max}$(cm$^{-1}$) |
|---|---|---|---|
| 2-Allylphenol | $0.46\pm0.14$ | $-0.49\pm0.22$ | 65.5 |
| 2-Benzylphenol | $0.33\pm0.05$ | $-0.53\pm0.10$ | 50.8 |
| 2-Isopropenylphenol | $0.76\pm0.11$ | $-1.17\pm0.20$ | 82.0 |
| 2-Hydroxybiphenyl | $1.45\pm0.27$ | $-0.17\pm0.42$ | 42.0 |

the frequencies of the internally interacting $\nu_{O-H}$ which has no available proton any longer also rise in the same way with the temperature and this fact may be explained from lessening of the dipole-dipole interaction between phenols and solvent molecules by their thermal motion, to which Cole and Macritchie⁹⁾ have recently alluded. About a half of the decrease in the total intensity can be attributed to the thermal expansion of the solvent, the volume expansion coefficient of carbon tetrachloride being 1.236 $\times 10^{-3}$.

In Table V are listed the energies of the interaction ($-\Delta H$), together with constant $\Delta S/R - \ln a$, obtained by applying Eq. 3 to the above data in Tables I to IV. The shifts (for the room temperature) of the $\nu_{O-H}$ absorption maxima of the interacting form from that of the free one are listed in the last column for comparison of the shifts with the energy.

$-\Delta H$'s are all smaller than the weakest one of the ordinary hydrogen bonding which ranges from 2.3 (NH···N) to 7 (FH···F) kcal./mol.¹⁰⁾ Even the strongest interaction of this kind ever measured, 2.5 kcal./mol. for 2-hydroxy-4-nitrobiphenyl²⁾, lies at the lowest limit of the energy for the hydrogen bonding. This difference in energy may be the best criterion which differentiates this interaction from the ordinary hydrogen bonding. It seems that at least no simple relation exists between $\Delta\nu_{\max}$ and $-\Delta H$. The rotational degree of freedom must be taken into account. In 2-allylphenol, 2-benzylphenol and 2-isopropenylphenol, a loss of energy may be caused by the formation of the internal interaction, because the molecule must take a structure, which is otherwise the sterically unfavored one. The apparent $-\Delta H$, therefore, does not necessarily mean the true energy difference of the interaction. These considerations lead to the reasonable explanation of the arbitrary relation between $\Delta\nu_{\max}$ and the energy difference. Some relation may be expected between $\Delta\overline{\nu_{\max}}$ and $-\Delta H$ if the compounds are limited to a certain series, but, it is still clear that the relation is not so simple as a linear one, as is understood from the three compounds in the biphenyl series. Hence, it is dangerous to evaluate the energy of the interaction from the mere comparison of the two frequencies.

Although, for strict understanding of the entropy changes of the interaction ($\Delta S$), another standard band common in frequency and in molecular absorption coefficient to both molecular types must be further used together with these two $\nu_{O-H}$'s, as shown by Mizushima and his collaborators¹¹⁾, constant $\Delta S/R - \ln a$ obtained by extrapolating $T$ to infinity in the Eq. 3 can be assumed to be a measure of the entropy change, since roughly speaking it can be assumed that constant $a$ in Eq. 2 is equal to unity, when $\ln a$ becomes zero. This assumption is partly supported by the speculation that the changes of the dipole moment accompanying the vibrational motion are much smaller, than in the case of the ordinary hydrogen bonding, and partly by the observation, that the total integrated intensities ($A_i + A_f$) in these phenols possessing different degrees of interaction are about equal to 1.5 $\times 10^4$ except that of 2-isopropenylphenol which is rather sterically hindered. Entropy changes accompanying the intramolecular interaction consist of those of the vibrational motion and of the internal rotation, each being estimated to be a few entropy units, when they are perfectly restricted¹¹,¹²⁾. With weak intramolecular interaction between the hydroxyl group and $\pi$-electrons this effect is expected to be less and it is the case in three of the phenols presented above. On the contrary, 2-isopropenylphenol shows an extraordinary great entropy term which can not be explained from the above factors only. It can be well explained by assuming that this phenol exists in four rather stable conformations near coplanarity, and only one of them can be the molecular form favorable for the interaction. Then the ratio of the number of the conformation, 1/3, must be introduced into the entropy term in the form of ln 3 and subtraction of the latter from the former gives a reasonable value ($-0.07$) comparable to the other phenols. Almost equal $\Delta S/R - \ln a$ values in 2-allylphenol and 2-benzylphenol can be understood by considering that the interaction in both cases will occur with the $\pi$-electron at the "$\beta$" carbon atom in respect of the phenol nucleus as already suggested in the previous paper¹⁾. The small $\Delta S/R - \ln a$ value in 2-hydroxybiphenyl is rather unexpected. One of the most interesting internal motions in this molecule is that of rotation and/or vibration around the pivot bond. This will give rise to an appreciable entropy decrease if perfectly restricted. The observed small amount of the entropy term shows that the contribution of this effect is very small, and the moderate changes in the O-H force constants between free and interacting forms can be accomodated with almost no entropy changes.

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12) H. H. Jaffé, ibid., **79**, 2373 (1957).

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