The Energy of the Intermolecular Interaction between the Proton of the OH Group and the π Electron of Some Compounds

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The OH infrared absorption bands of both inter- and intra-molecular interactions between the π electron and the proton of the OH group have been observed by many workers[1]. The energies of the intramolecular interaction between the π electron and the proton have also been measured for some typical compounds by Ōki and Iwamura[2]. However, so far little is known of the energy of the intermolecular interaction between the π electron and the proton.

It does not seem correct to calculate the intermolecular interaction energy simply from the frequency shift of the OH band by the use of Badger's postulation[3], in the same manner as Goldman and Crisler[4] tried in the case of intramolecular interaction. Since certain differences may exist between the inter- and intra-molecular interactions in the factors which contribute to the interaction energy of the proton and the π electron, that is, steric factors between the two interacting groups, the direction character of the π electrons, etc., it seems unreasonable to estimate the energy of the intermolecular interaction simply from the frequency shift relationship which is obtained in the case of intramolecular interaction.

In a series of previous papers[5] it has been shown that lignin is a very good reinforcer for some types of synthetic rubbers, and the mechanism of the interaction between these polymers has also been reported. The main object of the present study is to estimate the interaction energy between the π electron in synthetic rubbers (styrene-butadiene copolymer, SBR, and acrylonitrile-butadiene copolymer, NBR) and the proton of the OH groups in lignin. Since it is difficult to measure the interaction energy between these large molecules, simple molecules with similar chemical structures were chosen as model compounds. As the proton donor, phenol, catechol, vanillin and 3-phenylpropanol were used, and as the proton acceptor, isopropylbenzene, cyclohexene and isobutyronitrile were used.

The intermolecular interaction energies between the OH groups and the π-electrons of these model compounds were estimated from the variation with the temperature of the intensities of the OH absorption bands. Infrared absorption spectra were measured for the ternary system of the proton donor, the proton acceptor and the solvent (carbon tetrachloride).

Experimental

Measurement.—A Perkin-Elmer model 13 infrared spectrophotometer was used, with a lithium fluoride prism. The concentration of the proton donor in carbon tetrachloride was 0.015 mol./l. An absorption cell with potassium bromide windows was placed in an asbestos block equipped with a heating coil, and the temperature of the contents was kept at an appropriate temperature (within $\pm 1°C$) by controlling the electric current in the coil. The temperature was read by a thermometer inserted in a hole in the potassium bromide cell wall. Measurements of the infrared absorption of OH group were made at 25, 40 and 60°C.

Materials. — Phenol and 3-phenylpropanol were distilled in a vacuum. Vanillin was purified by sublimation, and catechol was purified by recrystallization.

Cyclohexane, isopropylbenzene and isobutyronitrile were dried and distilled through a short helix-packed column. Carbon tetrachloride, free of hydroxylic or other basic impurities, was dried and distilled before use.

Calculation.—In the calculation of the energy, it has been assumed that one proton donor molecule forms the hydrogen bond with one proton acceptor molecule and that the following equilibrium is maintained:

$$\text{Donor} + \text{Acceptor} \rightleftarrows \text{Complex}$$

$$K = [\text{C}]/([\text{D}]\cdot[\text{A}])$$

where, [D], [A] and [C] are the concentrations of donor, acceptor and complex, respectively, and K is the equillibrium constant. In order to simplify the calculation, the following assumptions were made:

a) $[\text{A}] \gg [\text{C}]$. Hence, [A] is almost constant and equal to $[\text{A}_0]$, the initial concentration of the acceptor.

b) [D] and [C] are proportional to the area intensities (S_D and S_C) of the free and bonded OH

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[1] R. West, *J. Am. Chem. Soc.*, **81**, 1615 (1958); P. R. Shleyler, O. S. Trifan and R. Bacskai, ibid., **80**, 6691 (1958). See also references cited there.

[2] M. Ōki and H. Iwamura, This Bulletin, 33, 717 (1960).

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

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

[5] S. Wada, *Chem. High Polymer* (*Kobunshi Kagaku*), **18**, 541 (1961); S. Wada, ibid., in press.

absorption bands respectively, and the proportional constants are defined as K_D and K_C. As an alternate assumption, [D] and [C] are proportional to the peak values of the molecular absorption coefficients (κ_D and κ_C) of the free and bonded OH absorption bands respectively, the proportional constants being K_D' and K_C'.

c) The changes of entropy and enthalpy in the formation of the bond remain constant throughout the temperature range of the measurement.

From these assumptions, it follows that

$$K=K_C\cdot S_C/K_D\cdot S_D\cdot[\mathrm{A}] \tag{2}$$

As

$$-\boldsymbol{R}T\ln K=\Delta H-T\Delta S \tag{3}$$

$$\ln K_{T_1}-\ln K_{T_2}=\ln(S_C/S_D)_{T_1}-\ln(S_C/S_D)_{T_2} = -\Delta H/\boldsymbol{R}(1/T_1-1/T_2) \tag{4}$$

Or,

$$K=K_C'\cdot\kappa_C/K_D'\cdot\kappa_D\cdot[\mathrm{A}] \tag{2'}$$

$$\ln K_{T_1}-\ln K_{T_2}=\ln(\kappa_C/\kappa_D)_{T_1}-\ln(\kappa_C/\kappa_D)_{T_2} = -\Delta H/\boldsymbol{R}(1/T_1-1/T_2) \tag{4'}$$

Therfore, the enthalpy change ΔH is calculated from the slope of the line obtained by plotting $\ln(S_C/S_D)$ or $\ln(\kappa_C/\kappa_D)$ versus $1/T$. The entropy change ΔS is calculated by Eq. 3, using the values of ΔH and K. In the previous studies[5], the value of the equilibrium constant, K, was obtained from the variation of the molecular absorption coefficient of the free OH band with the concentration of the acceptor.

When the bonded and the free OH absorption bands overlap, as is shown in Fig. 1, the areas of the two bands were estimated as follows: As shown in Fig. 1, the slope of the free OH absorption curve is assumed to be symmetric, and the area of the curve ABCDE is taken for that of the free OH band. The area of the curve EDCF is taken for that of the bonded OH band.

In the case of catechol, another OH absorption band, due to the intramolecular hydrogen bond, appears. However, its intensity remains almost unchanged throughout the temperature range of the measurement and remains almost unaffected even when mixed with the proton acceptor.

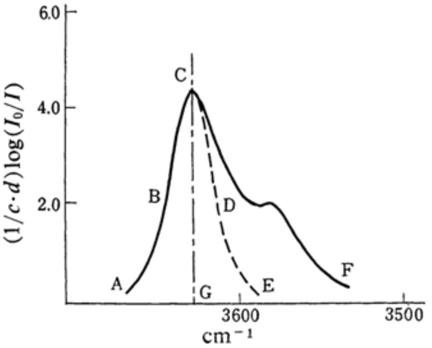

Fig. 1. The infrared absorption spectrum of OH group of 3-phenylpropanol (0.030 mol./l.) in the coexistence of cyclohexene (2.27 mol./l.) in CCl_4. The free OH band and intermolecularly bonded OH band are separated from each other by an extrapolated curve CDE.

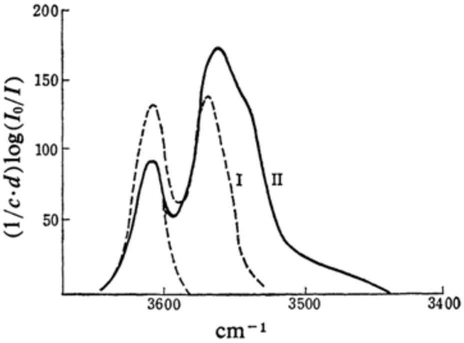

Fig. 2. The infrared absorption spectrum of OH group of catechol. I, 0.015 mol./l. in CCl_4; II, 0.015 mol./l. in CCl_4 in the coexistence of isopropylbenzene (1.80 mol./l.). The area of the intermolecularly bonded OH absorption band is estimated by subtracting the intramolecularly bonded OH absorption I from the absorption curve II.

The intensity ratio of the intramolecularly bonded and the free OH absorption bands is independent of the temperature, being 1.17 at 25°C and 1.12 at 60°C. Moreover, the intensity of the intramolecularly bonded OH absorption band remained almost unaffected even when the amount of free OH decreased very much under the coexistence of isobutyronitrile, the strongest proton acceptor in the present investigation. So, when the inter- and intra-molecularly bonded bands are overlapped, they were separated from each other in a manner similar to that described above by drawing the same intramolecularly bonded absorption curve as in the absence of the acceptor (Fig. 2).

Results and Discussion

The enthalpy change, ΔH, obtained from the slope of the line of the plot of $\ln(S_C/S_D)$ or $\ln(\kappa_C/\kappa_D)$ versus $1/T$, and the entropy change, ΔS, calculated by substituting the values of K and ΔH in Eq. 3, are tabulated in Table I. Generally, when isopropylbenzene is used as an acceptor, the frequency shifts, $-\Delta H$ and $-\Delta S$, are all lower than when cyclohexene is used. This is considered to result from the fact that in isopropylbenzene the degree of localization of the π electrons is lower due to the conjugation in benzene ring and the fact that the proton accepting field is larger, so that the degree of freedom of the complex is greater. When cyclohexene and isobutyronitrile are used as acceptors, $-\Delta S$ are approximately equal to the normal value, 13 e. u., for the ordinary intermolecular hydrogen bond[6,7], while when isopropylbenzene is used, the $-\Delta S$ are generally smaller, as has been stated above, and they amount to as small values as

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6) H. Tsubomura, *J. Chem. Phys.*, **23**, 2130 (1955).
7) H. H. Jaffé, *J. Am. Chem. Soc.*, **79**, 2373 (1957).

TABLE I. SOME THERMODYNAMIC VALUES OF THE INTERMOLECULAR HYDROGEN BOND BETWEEN PROTON AND π ELECTRON

Donor	Acceptor	$\Delta\nu$ cm^{-1}	K l./mol.		25°C	40°C	60°C	$-\Delta H$ kcal./mol.	$-\Delta S$ e. u.
Phenol	Cyclohexene	97	0.230	κ_C/κ_D	0.377	0.332	0.243	2.83	12.8
(0.015 mol./l.)	(2.27 mol./l.)			S_C/S_D	1.51	1.13	0.819	3.40	14.9
Phenol	Isopropylbenzene	57	0.320	κ_C/κ_D	1.98	1.57	1.32	2.60	10.9
(0.015 mol./l.)	(3.60 mol./l.)			S_C/S_D	2.65	2.40	2.07	1.40	7.02
Catechol	Cyclohexene	129	0.232	κ_C/κ_D	0.825	0.587	0.521	2.96	12.9
(0.015 mol./l.)	(2.27 mol./l.)			S_C/S_D	0.825	0.570	0.40	3.80	15.8
Catechol	Isopropylbenzene	72	0.100	κ_C/κ_D	1.378	1.08	0.851	2.68	11.1
(0.015 mol./l.)	(1.80 mol./l.)			S_C/S_D	2.402	2.16	1.81	1.60	7.82
Catechol	Isobutyronitrile	194	9.10	κ_C/κ_D	2.44	1.71	1.08	4.82	12.0
(0.015 mol./l.)	(0.15 mol./l.)			S_C/S_D	11.43	7.16	5.14	4.60	11.1
Vanillin	Cyclohexene	50	0.076	κ_C/κ_D	0.116	0.10	0.097	1.74	11.2
(0.015 mol./l.)	(2.27 mol./l.)			S_C/S_D	0.34	0.295	0.256	1.56	10.8
Vanillin	Isopropylbenzene	33	0.105	κ_C/κ_D	0.383	0.365	0.337	0.62	6.72
(0.015 mol./l.)	(3.60 mol./l.)			S_C/S_D	0.367	0.308	0.277	1.40	9.34
Vanillin	Isobutyronitrile	143	0.87	κ_C/κ_D	0.776	0.577	0.444	3.50	12.3
(0.015 mol./l.)	(2.40 mol./l.)			S_C/S_D	—	—	—	—	—
3-Phenylpropanol	Cyclohexene	48	0.083	κ_C/κ_D	0.830	0.767	0.687	1.2	9.15
(0.030 mol./l.)	(2.27 mol./l.)			S_C/S_D	0.950	0.830	0.764	1.2	9.12
3-Phenylpropanol	Isopropylbenzene	30	0.138	κ_C/κ_D	0.765	0.705	0.654	0.8	6.75
(0.030 mol./l.)	(1.80 mol./l.)			S_C/S_D	0.785	0.726	0.650	1.0	7.31
3-Phenylpropanol	Isobutyronitrile	82	0.79	κ_C/κ_D	1.56	1.13	0.90	3.2	11.6
(0.030 mol./l.)	(0.60 mol./l.)			S_C/S_D	4.064	2.86	1.97	3.2	11.6

6~7 e. u. Such small values are also observed in some weak hydrogen bonds, such as those existing in the combinations of *o*-chlorophenol-methyl acetate[7] or chloroform-acetone[9].

Considering from the values of ΔH and ΔS for vanillin, the guaiacyl OH group seems to be able to form a stronger hydrogen bond with the π electron when a carbonyl group is present at the para position. Such a characteristic difference between a simple guaiacyl OH group and that having a carbonyl group in its para position for the hydrogen bond formation, has been observed by Lindberg[9] in a similar case of the interaction of various guaiacyl compounds and dioxane. The ability of the free OH group of catechol to form a hydrogen bond with the π electron is much larger than that of simple phenol, which is quite parallel to the case of the formation of an ordinary hydrogen bond.

The values of $-\Delta H$ for the intermolecular hydrogen bond between the OH groups and the π electron obtained in our present investigation are larger than those obtained by Ōki and Iwamura[2] for intramolecular hydrogen bonds. This may be explained by considering that the steric stress may influence the formation of the intramolecular hydrogen bond. For example, in *o*-allylphenol, the direction of the π electron orbital of an allyl group seems to be difficult to orient towards the favorable direction for the interaction with the phenolic OH group in its ortho position, probably because in being compelled to be oriented parallel to the direction of the π electron of the benzene ring, they repulse each other. Consequently, it is to be expected that the steric condition for the formation of the bond

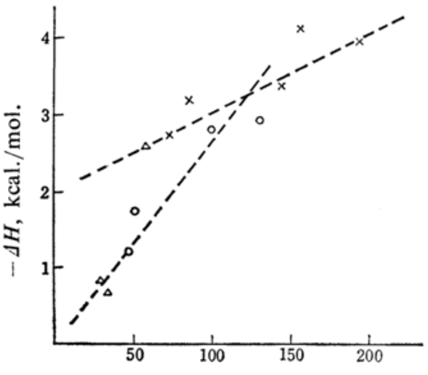

Fig. 3. The relation between $\Delta\nu$ and $-\Delta H$ (1), being used $-\Delta H$ values obtained from the slope of the line $\ln(\kappa_C/\kappa_D)$ versus $1/T$.

× : In the case of isobutyronitrile as acceptor.
○ : In the case of cyclohexene as acceptor.
△ : In the case of isopropylbenzene as acceptor.

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[8] S. Nagakura, ibid., 76, 3070 (1954).

[9] C. M. Huggins and G. C. Pimentel, *J. Chem. Phys.*, 23, 1244 (1955).

[10] J. J. Lindberg, *Societas Scientiarum Fennica, Commentationes Physico-Mathematicae XX*, 1 (1957).

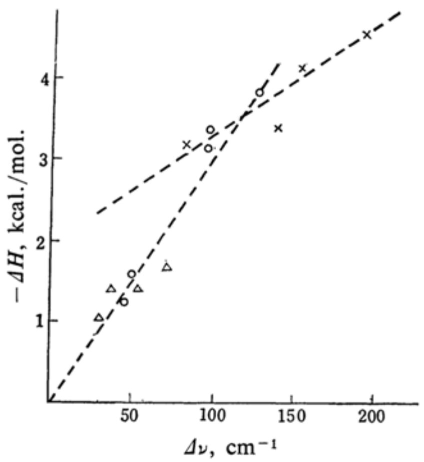

Fig. 4. The relation between $\Delta\nu$ and $-\Delta H$, being used $-\Delta H$ values obtained from the slope of the line $\ln(S_C/S_D)$ versus $1/T$.

× : In the case of isobutyronitrile as accepter.
○ : In the case of cyclohexene as acceptor.
△ : In the case of isopropylbenzene as acceptor.

is more favorable in the intermolecular interaction than in the intramolecular interaction.

When two acceptors, isobutyronitrile and cyclohexene, are compared, there is no great difference in $-\Delta H$. This is approximately 1 kcal./mol. Therefore, the proton-accepting character of the nitrile group is not always attributable only to the electronegativity of the nitrogen atom, but also rather reasonably to that of the π electron of the triple bond in the nitrile group.

In Figs. 3 and 4 are shown the relations between $-\Delta H$ and the frequency shift $\Delta\nu$. The $-\Delta H$ values in Figs. 3 and 4 are calculated from κ_C/κ_D and S_C/S_D respectively. As seen from these figures, the relations between these two quantities are not linear, which is contrary to Badger's postulation. It seems to be more reasonable to divide the curves into two linear portions:

for $\Delta\nu < 100\ \text{cm}^{-1}$;

$$-\Delta H \fallingdotseq \Delta\nu/30\ \text{kcal./mol.}$$

and for $\Delta\nu > 100\ \text{cm}^{-1}$;

$$-\Delta H \fallingdotseq 2.0 + \Delta\nu/70\ \text{kcal./mol.}$$

The slope in the region of $\Delta\nu < 100\ \text{cm}^{-1}$ is considerably greater than that obtained by Badger[2] for ordinary hydrogen bonds.

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