The Interaction between the Proton of the Carboxyl Group and the π Electron of Some Compounds

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The hydrogen bond between the proton and the π electron has been studied mainly by investigating the variation of the infrared absorption of the OH or NH group due to the interaction between the proton of these groups and the π electron. The frequency shift of the OH absorption band increases in proportion to the proton-donating power of these groups, as was observed by West[1]. The author[2] has established that the larger the frequency shift, the stronger the hydrogen bond in the intermolecular interaction between the proton and the π electron is; this was established by using compounds having an OH group such as phenol, vanillin, catechol, 3-phenylpropanol as proton donors and some compounds having π electrons such as cyclohexene, isopropylbenzene, isobutyronitrile as proton acceptors. Therefore, the formation of the stronger hydrogen bond may be expected between the π electron and the proton of the carboxyl group, because the proton-donating power of this group is much larger than that of the other ordinary proton donor groups such as OH or NH. So far, however, no investigation on the interaction between the π electron and the proton of a carboxyl group has been made.

1) R. West, *J. Am. Chem. Soc.*, **81**, 1615 (1958).
2) S. Wada, This Bulletin, **35**, 707 (1962).

In the present report, therefore, the interaction between the proton of the carboxyl group of benzoic acid or cinnamic acid, and the π electron of squalene, toluene, or acetonitrile, has been investigated by measurement of the infrared spectra. The main purpose of this investigation is, in connection with the previous one[2], to learn the nature of the secondary bond of the π electron of some synthetic rubbers (such as styrene-butadiene copolymer, SBR, and acrylonitrile-butadiene copolymer, NBR) and the proton of the carboxyl group of thiolignin, which is a good reinforcer for these rubbers.

Experimental

The infrared absorption spectra were measured with a Perkin-Elmer model 13 spectrophotometer with a lithium fluoride prism. The slit width was 70 μ. The absorptions of the solutions of binary systems (a) of acid and carbon tetrachloride and of ternary systems (b) of acid, carbon tetrachloride and a proton-accepting compound (squalene, toluene or acetonitrile) were measured, together with those of the corresponding solvents. The sample solution was placed in a quartz cell 10 mm. in length. The absorbance, $\log I_0/I$, of acid was obtained by subtracting the absorbance of the solvent from that of the solution containing acid. The concentrations of acids are 0.003 and 0.007 mol./l. The two absorption curves, a and b, thus obtained were compared, and the frequency shift of the OH band by hydrogen bonding was estimated from the position of the OH band in the carboxyl group of the acid monomer molecule.

The chemicals used were purified according to the usual methods; their phyical constants were as follows: Benzoic acid, m.p. 121~122°C; cinnamic acid, m.p. 135~136°C; squalene, b.p. 238~240°C/2 mmHg; toluene, b.p. 110.5°C; acetonitrile, b.p. 81.6°C.

Results

The absorption spectra of benzoic acid in the mixture of carbon tetrachloride and a proton-accepting compound in the region of the OH absorption of the carboxyl group of monomeric acid molecule are shown in Figs. 1—3, together with those in pure carbon tetrachloride. Similar absorption spectra were obtained in the case of cinnamic acid. The absorption was measured also towards the region of the OH frequency of the dimeric acid molecule as far as 2400 cm^{-1}, but the difference between binary (a) and ternary (b) systems could not but be ambiguous because of the presence of the intense C–H band in the region of the OH absorption of the dimeric acid. However, in the case of acetonitrile, which is more powerful in proton-accepting power compared with the other two, squalene and toluene, this difference was observed, as is shown in Fig. 4.

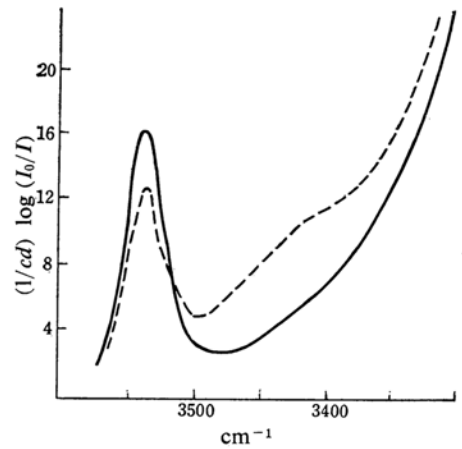

Fig. 1. Infrared absorption spectra of benzoic acid (0.007 mol./l.): a, in CCl_4; b, in the mixture of squalene and CCl_4. (The concentration of squalene is 0.5 mol./l.)
Note: $(1/cd)\log(I_0/I)$, molecular absorption coefficients. (c, concentrations in mol./l.; d, path length in cm.).
—— a ····· b

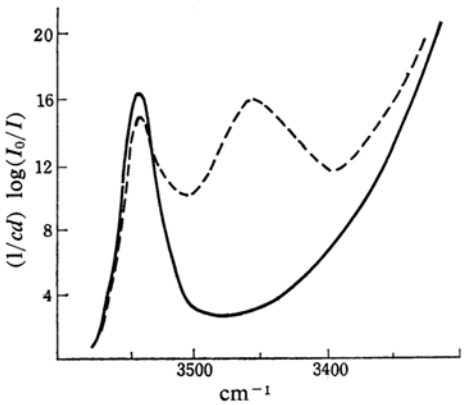

Fig. 2. Infrared absorption spectra of benzoic acid (0.007 mol./l.): a, in CCl_4; b, in the mixture of $C_6H_5CH_3$ and CCl_4. (The concentration of $C_6H_5CH_3$ is 3 mol./l.)
—— a, ····· b

The frequency shifts of the OH band of carboxyl groups due to the formation of the hydrogen bond with the π etectron are shown in Table I, with reference to those of some phenolic hydroxyl groups as proton donors, reported on in the previous paper[2]. The frequency shifts are much larger in the case of acid than in the case of phenol and even catechol, although the same proton acceptor was not used in both cases.

The maximum of the OH absoption curve when squalene is used as a proton acceptor is not so clear as in the case of the other two

TABLE I. THE ENERGY OF THE HYDROGEN BOND BETWEEN PROTON AND π ELECTRON (kcal./mol.)

Acceptor		Donor			
		Vanillin	Catechol	Benzoic acid	Cinnamic acid
ν_0		3538	3610	3542	3545
Cyclohexene	$\Delta\nu$	50	129		
	ΔE	1.56*	3.80*		
Squalene	$\Delta\nu$	60	150	217	215
	ΔE	2.08	4.2	5.0	5.0
Isopropylbenzene	$\Delta\nu$	33	72		
	ΔE	1.40*	2.68*		
Toluene	$\Delta\nu$			92	82
	ΔE			3.3	3.2
Isobutyronitrile	$\Delta\nu$	143	192		
	ΔE	3.50*	4.6*		
Acetonitrile	$\Delta\nu$	140		267	255
	ΔE	3.50		5.8	5.6

ΔE*, actually measured values, in the previous investigation[2].

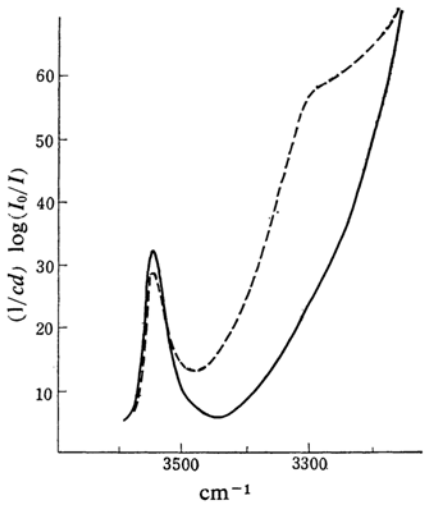

Fig. 3. Infrared absorption spectra of benzoic acid (0.003 mol./l.): a, in CCl_4; b, in the mixture of CH_3CN and CCl_4. (The concentration of CH_3CN is 0.3 mol./l.)
—— a, ····· b

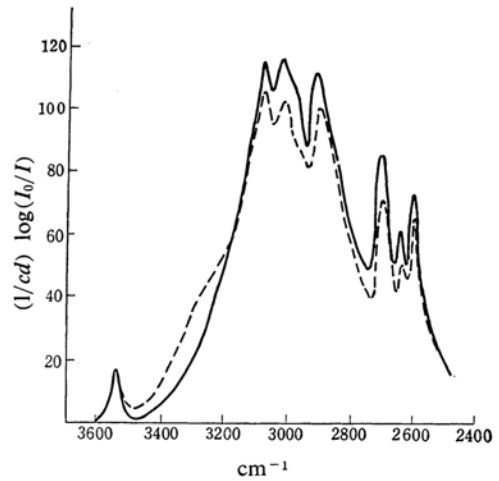

Fig. 4. Infrared absorption spectra of benzoic acid (0.007 mol./l.): a, in CCl_4; b, in the mixture of CH_3CN and CCl_4. (The concentration of CH_3CN is 0.3 mol./l.)
—— a, ····· b

proton acceptors, toluene (Fig. 2) and acetonitrile (Fig. 3). This may mean that the proton-accepting character of the π electron in each double bond of the squalene molecule, which has five double bonds, is not always the same. Such a tendency may be much greater when the proton acceptor molecule is so large as a rubber molecule.

Even when the concentration of the acid in carbon tetrachloride is so dilute as 0.003 mol./l. or 0.007 mol./l., most parts of the acid exist in the state of dimer, and when a proton-accepting compound is added to this carbon tetrachloride solution of acid, the concentrations of both monomer and dimer change, because they are affected by the formation of the hydrogen bond between the proton of the carboxyl group and the π electron of the proton acceptor and by the increase of the dielectric constant of the medium around the acid molecule. Therefore, both the equilibrium constant of the formation of the hydrogen bond and the energy of the hydrogen bond are difficult to determine. However, the energy may be expected to be considerably large, in view of the fact that the frequency shift of the OH absorption of the carboxyl group is larger than that of catechol and that, consequently, its free OH group forms a stronger hydrogen bond with the π electron, as is shown in Table I.

In row ΔE of this table there are presented the energies of the hydrogen bond between the proton of the carboxyl group and the π electron calculated from the frequency shift

on the assumption that the following linear relationship between the frequency shift ($\Delta\nu$) of the OH group and the hydrogen bond energy (ΔE), that relationship reported in the previous paper[2], is also applicable in the present case:

$$\Delta E = 2.0 + \Delta\nu/70 \quad \text{kcal./mol.}$$

From the above result, it is concluded that there is a possibility of interaction between the π electron in a rubber molecule and the proton of a carboxyl group existing in a free state at the surface of a lignin particle in a lignin-rubber (SBR or NBR) compound. Therefore this interaction seems to contribute greatly to the secondary bond between lignin and rubber. The fact that the air-oxidated thiolignin, having a larger number of carboxyl groups, has a much higher reinforcing power on synthetic rubbers than ordinary untreated thiolignin may also be explained by the enhancement of the interaction between the π electron in synthetic rubbers and the carboxyl groups in oxidized thiolignin.

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3) R. A. V. Raff and O. H. Tomlinson, *Rubber Age*, 64, 197 (1948); U. S. Pat. 2610954 (1952).