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An Infrared Spectroscopic Study of Hydrogen Bonding Interaction. Structural Studies of Proton-donating and -accepting Powers

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The relationship between the proton-donating and proton-accepting powers and the structures of various proton donors and acceptors was studied in the liquid phase by means of an infrared spectrophotometer. The proton-donating powers of the donors were evaluated by means of the ratios of the O–H shifts of the donors (RO–H) to those of methanol in various proton acceptor solutions. The proton-accepting powers of the acceptors were evaluated by means of the division of the O–H shifts by the proton-donating powers of the donors used. The proton-donating powers increased with the decrease in the pK_a or the ionic RO–H bond dissociation energies and with the increase in the electron affinities of RO radicals, *i. e.*, *t*-butanol$<$methanol$\ll$trimethylsilanol$<$phenol$<$*p*-nitrophenol. In a homologous series, the proton-accepting powers increased with the decrease in the ionization potentials. In the case of the aromatic ethers with two proton accepting sites, two characteristic O–H vibrational bands were observed. The difference in the proton-accepting powers of the vinyl and ethyl compounds with the same substituent was observed, and the π-electron-mobility index, which was considered to be a measure of the energy level of the π-electrons of the vinyl group, was defined and discussed.

Since the hydrogen bond was first recognized, great attention has been paid to the physicochemical behavior of many types of polar compounds.[1] Enormous studies dealing with the intra- and intermolecular hydrogen bond have been made by many researchers from the theoretical and the experimental aspects; they were summarized by Pimentel *et al.*[2,3] However, the main studies in this field have been focused on the physical properties of liquid and crystal states, except for the gaseous adsorption on a solid.[4,5]

In our previous papers,[6–8] we have concluded that the shifts of the O–D or the C=O vibrational bands of monodeuteromethanol as a proton donor, or of acetophenone as a proton acceptor, in various liquid organic compounds can be regarded as a measure of the electron-donating powers, or of the electron-accepting powers, of compounds respectively.

The objective of the present spectroscopic work is to discuss quantitatively the relationship between the proton-donating and proton-accepting powers and the structures or the electronic natures of various proton donors and acceptors. Moreover, on the basis of the experimental results of the proton-accepting powers of the vinyl and ethyl compounds with the same substituent, the π-electron-mobility index, as a measure of the energy level of the π-electrons of the vinyl group, will be defined and discussed.

Experimental

Materials. Methanol, monodeuteromethanol, *t*-butanol, phenol, *p*-nitrophenol, and trimethylsilanol were used as the proton donors. All the compounds but trimethylsilanol were obtained commercially and were purified by distillation or recrystallization. The trimethylsilanol was synthesized by the method of Sommer.[9]

Apparatus and Method. A small quantity (0.03—0.08 mol/*l*) of the proton donor was added to 1.0 m*l* of the proton acceptor in a weighing bottle. After the

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[1] W. Gordy and S. C. Stanford, *J. Chem. Phys.*, **9**, 204 (1941).

[2] E. R. Lippincott and R. Schroeder, *ibid.*, **23**, 1099 (1955). N. D. Coggeshall, *ibid.*, **18**, 978 (1950); Z. Yoshida and E. Osawa, *J. Amer. Chem. Soc.*, **87**, 1467 (1965); A. Allerhand and P. von R. Schleyer, *ibid.*, **85**, 371 (1963).

[3] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Company, San Francisco and London, 1960.

[4] J. Donohue, *J. Phys. Chem.*, **56**, 502 (1952).

[5] A. V. Kiselev and V. I. Lygin, "Infrared Spectra of Adsorbed Species," ed. by L. H. Little, Academic Press, London and New York (1966), p. 274.

[6] T. Kagiya, Y. Sumida and T. Inoue, This Bulletin, **41**, 767 (1968).

[7] T. Kagiya, Y. Sumida and T. Inoue, *ibid.*, **41**, 773 (1968).

[8] T. Kagiya, Y. Sumida and T. Inoue, *ibid.*, **41**, 779 (1968).

[9] L. H. Sommer, E. Pietrusza and F. C. Whitmore, *J. Amer. Chem. Soc.*, **68**, 2282 (1946).

Table 1. Frequency shifts of O–H vibrational bands of various proton donors in proton acceptor solutions (cm^{-1})

	t-Butanol		Methanol		Trimethylsilanol		Phenol		*p*-Nitrophenol		Monodeuteromethanol[a]	
	ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$
Chloroform	3605	−15	3642	−19	3668	−26	3608	−40	3594	−59	2679	−11
Benzene	3590	0	3623	0	3642	0	3568	0	3535	0	2668	0
Ethyl acetate	3541	49	3561	62	3540	102	3434	134	3356	179	2628	40
Acetonitrile	3533	57	3551	72	3524	118	3411	157	3321	214	2613	55
Diethyl ether	3506	84	3516	107	3464	178	3341	227	3218	317	2589	79
1,4-Dioxane	3503	87	3515	108	3466	176	3340	228	3219	316	2593	75
Tetrahydrofuran	3492	98	3495	128	3430	212	3300	268	3180	355	2578	90

a) See Ref. 6.

bottle had then been shaken for 10 min at room temperature (20±3°C), the mixture was used for the measurement of the infrared spectrum. All the spectral measurements were made in the O–H (or O–D) fundamental region, using a Japan Spectroscopic Co. Model DS-402G or DS-403G infrared spectrophotometer. The thickness of the KBr fixed cell used was 0.010 cm. The dependence of the concentration of the proton donor on the shift of the O–H (or O–D) band was negligible in this concentration range. The experimental error in the measured shifts of the O–H (or O–D) bands was not more than ±1.0 cm^{-1}.

Results and Discussion

Proton-donating Powers and Proton-accepting Powers. The positions of the unassociated hydroxyl fundamental vibrational bands of various proton donors involved in several proton acceptor solutions are summarized in Table 1. According to the definition of the electron-donating powers of compounds presented in a previous paper,$^{6)}$ the relative differences in the O–H frequency shifts of the proton donors (RO–H) observed in the proton acceptor solutions from that in benzene were calculated:

$$\Delta\nu_{\text{RO-H}}(\text{proton acceptor}) = \nu_{\text{RO-H}}(\text{benzene}) - \nu_{\text{RO-H}}(\text{proton acceptor}) \qquad (1)$$

Obviously, the magnitudes of the O–H frequency shifts are due to the relative strengths of the intermolecular interaction between the proton donors and the proton acceptors, *i. e.*, the proton-donating powers and the proton-accepting powers.

In order to evaluate quantitatively the proton-donating powers of proton donors with the use of the definition expressed by Eq. (1), the O–H frequency shifts of the proton donors in several acceptor solutions were plotted against those of methanol in the same solution. As is shown in Fig. 1, linear relations with different slopes were found between them. The slopes are obviously the characteristic values, depending only on the structures of the proton donors, not on those of the proton acceptors.

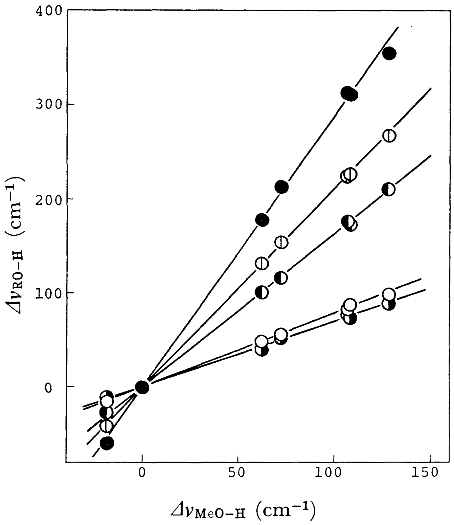

Fig. 1. O–H Frequency shifts of the proton donors in the typical proton acceptor solutions and O–H frequency shifts of methanol in the same solutions. Proton donor: ◑, Monodeuteromethanol; ○, *t*-Butanol; ◐, Trimethylsilanol; ⦶, Phenol; ●, *p*-Nitrophenol

Therefore, we believe that the values of the (Φ_D) slopes, which represent the magnitudes of the O–H shifts of the proton donors relative to that of methanol as a standard proton donor, indicate a quantitative measure of the proton-donating powers:

$$\Phi_D = \frac{\Delta\nu_{\text{RO-H}}}{\Delta\nu_{\text{MeO-H}}} \qquad (2)$$

On the basis of the same consideration, we defined the proton-accepting powers of proton acceptors (Φ_A), independent of the kind of proton donors, as the division of the O–H shifts of a certain proton donor in the proton-acceptor solutions by the Φ_D of the proton donor, as follows:

$$\Phi_A = \frac{\Delta\nu_{\text{RO-H}}(\text{proton acceptor})}{\Phi_D} \qquad (3)$$

TABLE 2. COMPARISON OF PROTON-DONATING POWERS OF PROTON DONORS RO–H WITH RADICAL- AND IONIC-DISSOCIATION ENERGIES OF RO–H BONDS AND ELECTRON AFFINITIES OF RO RADICALS

Proton Donor RO–H	Φ_D	pK_a	D(RO–H) (kcal/mol)	D(RO$^-$–H$^+$)[a] (kcal/mol)	EA(RO)[b] (kcal/mol)
t-Butanol	0.79	19	105	325	56
Methanol	1.00	16	100	315	61
Trimethylsilanol	1.65	11	88[c]	295[c]	69
Phenol	2.13	10	84	290	70
p-Nitrophenol	2.92	7.1	75[c]	276[c]	75
Monodeuteromethanol	0.71	—	102	—	61

a) Values estimated by using $D(\mathrm{RO^-}–\mathrm{H^+})=D(\mathrm{RO–H})+IP(\mathrm{H})-EA(\mathrm{RO})$.
b) Values estimated from the pK_a values. See Ref. 11.
c) Approximate values.

It is obvious from this definition (3) that the proton-accepting powers should be equal to the O–H frequency shifts of methanol as a standard proton donor.

Proton-donating Powers and the Structures of Proton Donors. The acid-dissociation constant (pK_a) of the proton donor in an aqueous solution corresponds to the free-energy change of the equilibrium reaction to form the hydrated proton and corresponding anion; therefore, the pK_a is a thermodynamic measure of the proton-donating powers. As Fig. 2 shows, the Φ_D increases with the decrease in the pK_a[3,10] By using the pK_a values of the proton donors, the Φ_D value and then the O–H frequency shifts can be approximately predicted. The unknown values of pK_a can also be estimated from the frequency shifts.

In Table 2, the dissociation energies, D(RO–H), the ionic-dissociation energies, D(RO$^-$–H$^+$), of the RO–H bonds of the proton donors, and the electron affinities, EA(RO), of the RO radicals are listed. A correlation between the Φ_D and the ionic-dissociation energies of the RO–H bonds is illustrated in Fig. 3; the Φ_D becomes larger as the ionic-dissociation energy decreases. It can also be seen that, for the proton donors employed, the Φ_D increases with the increase in the electron affinity of the RO radical and the decrease in the dissociation energy of the

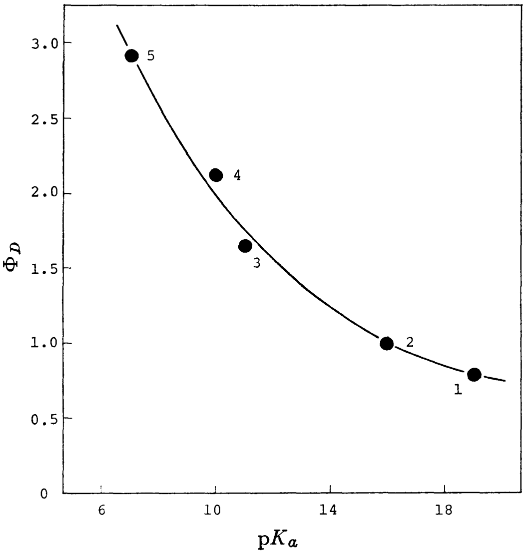

Fig. 2. Relation between the proton-donating powers Φ_D and the acid dissociation constants pK_a of proton donors.
Proton donor: 1, *t*-Butanol; 2, Methanol; 3, Trimethylsilanol; 4, Phenol; 5, *p*-Nitrophenol

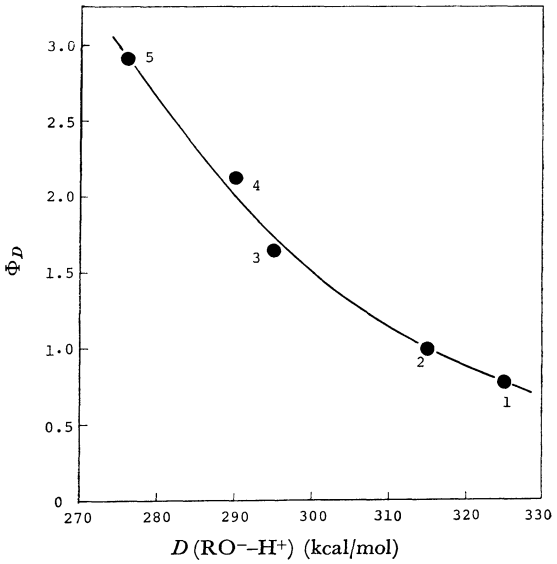

Fig. 3. Relation between the proton-donating powers Φ_D and the ionic-dissociation energies D(RO$^-$–H$^+$) of proton donors RO–H.
Proton donor: 1, *t*-Butanol; 2, Methanol; 3, Trimethylsilanol; 4, Phenol; 5, *p*-Nitrophenol

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[10] C. M. Huggins and G. C. Pimentel, *J. Phys. Chem.*, **60**, 1615 (1956).

RO–H bond. However, although the dissociation energies of the C–H bonds are slightly smaller than those of the RO–H bonds, the hydrocarbons have little proton-donating properties. This is due to the smaller electron affinities (12∼25 kcal/mol) of the hydrocarbon radicals, compared with those (55∼75 kcal/mol) of the RO radicals. It may be concluded from these considerations that the proton-donating powers, Φ_D, are mainly affected by the electron affinities of the RO radicals rather than by the dissociation energies of the RO–H bonds.

Moreover, in order to examine the isotope effect on the proton-donating powers, we compared the shifts of methanol and monodeuteromethanol. As is shown in Table 2, the values of Φ_D should fall to about 0.7 times by deuteration; this agreed well with the theoretical prediction proposed by Coggeshall.2)

Proton-accepting Powers and the Structures of Proton Acceptors. When trimethylsilanol was used as a proton donor, the O–H vibrational bands were sharp and symmetrical in all of the proton

TABLE 3. FREQUENCY SHIFTS OF O–H VIBRATIONAL BANDS OF TRIMETHYLSILANOL IN VARIOUS PROTON ACCEPTOR SOLUTIONS AND PROTON-ACCEPTING POWERS OF PROTON ACCEPTORS

Proton acceptor	$\nu_{\text{RO-H}}$ (cm^{-1})	$\Delta\nu_{\text{RO-H}}$ (cm^{-1})	$\Delta\nu_{\text{MeO-D}}$a) (cm^{-1})	Φ_Ab) (cm^{-1})
Aliphatic Hydrocarbons and Derivatives				
Chloroform	3668	−26	−11	−16.8
Aromatic Hydrocarbons and Derivatives				
Benzene	3642	0	0	0
Toluene	3636	6	2	3.2
Ethylbenzene	3631	11	4	6.2
m-Xylene	3630	12	7	8.6
Chlorobenzene	3662	−20	−8	−11.7
Anisole	3620, 3533c)	22, 109c)	—	13.3, 66.1c)
Phenetole	3621, 3542c)	21, 100c)	—	12.7, 60.6c)
Styrene oxide	3615, 3528c)	27, 114c)	—	16.4, 69.1c)
Esters				
Ethyl acetate	3540	102	40	59.2
Methyl propionate	3549	93	33	51.5
Vinyl acetate	3576	66	25	37.7
Methyl acrylate	3551	91	30	48.8
Nitriles				
Acetonitrile	3524	118	55	73.7
Propionitrile	3526	116	52	71.9
Acrylonitrile	3545	97	38	56.3
Ketones				
Acetone	3532	110	64	78.5
Methyl ethyl ketone	3534	108	57	73.0
Methyl vinyl ketone	3480	162	89	112.0
Ethers				
Diethyl ether	3464	178	79	108.8
Di-*n*-propyl ether	3459	183	73	107.0
n-Butyl ethyl ether	3456	186	77	110.8
1,2-Dimethoxyethane	3470	172	71	102.3
Ethyl vinyl ether	3553	89	35	51.7
n-Butyl vinyl ether	3554	88	33	50.0
Diallyl ether	3475	167	66	97.3
Propylene oxide	3508	134	59	82.3
Epichlorohydrin	3539	103	49	65.8
Tetrahydrofuran	3430	212	90	127.9
1,4-Dioxane	3466	176	75	106.9
Furan	3638	4	2	2.6

a) Data in Ref. 6 and the remeasured values.
b) Average values of Φ_A obtained from the different proton donors.
c) the OH vibrational band with the higher intensity.

acceptor solutions except in case of the aromatic ether solutions. The experimental data are summarized in Table 3.

In the aromatic hydrocarbons, it is observed that the introduction of electron-withdrawing groups or of electron-relieving groups to the benzene rings results in a decrease or an increase in the proton-accepting powers. For the aromatic ethers, represented by anisole, two unassociated O–H vibrational bands were observed. It is known that one showing the larger shift and intensity is to be assigned to the hydrogen bond formed by the lone-pair electrons of ether oxygen, while the other, showing the smaller shift and intensity, is to be assigned to the bond formed by the benzene ring.*[1]

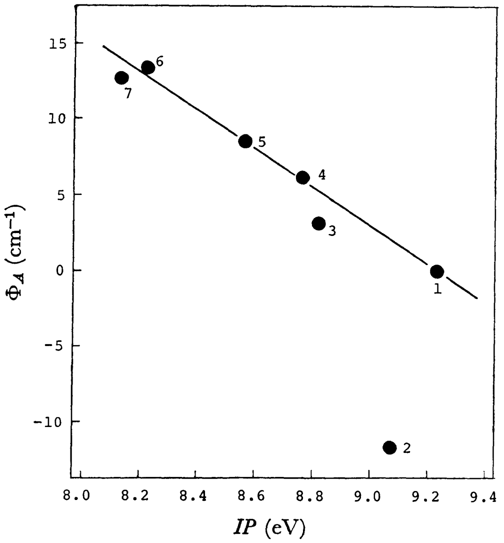

Fig. 4. Relation between the proton-accepting powers Φ_A and the ionization potentials of benzene derivatives.

Benzene derivative: 1, Benzene; 2, Chlorobenzene; 3, Toluene; 4, Ethylbenzene; 5, *m*-Xylene; 6, Anisole; 7, Phenetole

In order to determine a correlation between the proton-accepting powers, Φ_A, and the electronic natures of benzene derivatives, the Φ_A was plotted against the ionization potential. As is shown in Fig. 4, a linear relationship with a negative slope was observed between them. If the first ionization of the benzene derivatives is caused by the benzene ring, the results in Fig. 4 should indicate the intermolecular interaction between the silanol proton and the π-electrons on the benzene ring. Similarly, a straight line with a negative slope was also drawn between the Φ_A and the Hammett substituent constants (Fig. 5). This fact also supports the above consideration.

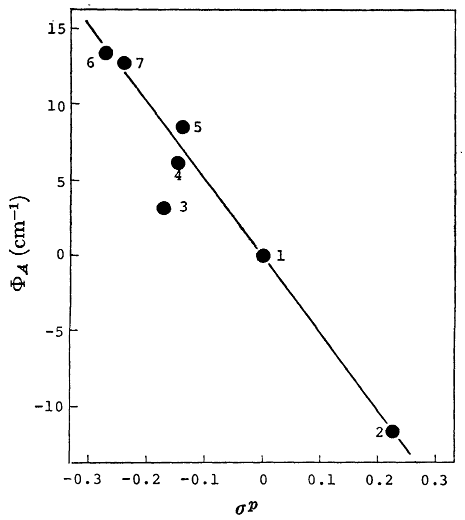

Fig. 5. Relation between the proton-accepting powers Φ_A and the Hammett substituent constants σ^p of benzene derivatives.

Benzene derivative: 1, Benzene; 2, Chlorobenzene; 3, Toluene; 4, Ethylbenzene; 5, *m*-Xylene; 6, Anisole; 7, Phenetole

On the other hand, it is of interest to ascertain information on the electronic state of the π-electrons, not only on the benzene ring, but also on the vinyl groups of vinyl compounds. From this point of view, the Φ_A values of a pair of the proton acceptors (CH_2=CHY and CH_3CH_2Y) with analogous chemical structures were compared as an example, methyl

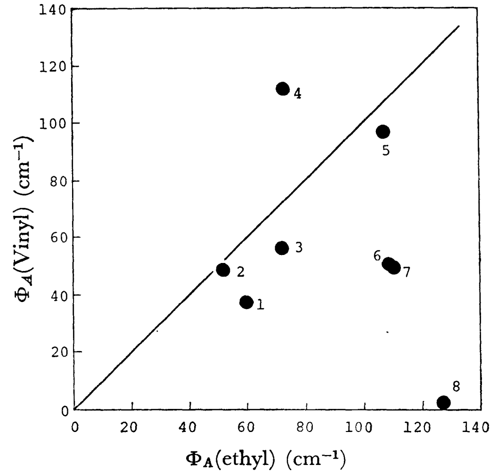

Fig. 6. Plots of the proton-accepting powers Φ_A (vinyl) of vinyl compounds *versus* the proton-accepting powers Φ_A(ethyl) of ethyl compounds.

Vinyl compound–Ethyl compound: 1, Vinyl acetate–Ethyl acetate; 2, Methyl acrylate–Methyl propionate; 3, Acrylonitrile–Propionitrile; 4, Methyl vinyl ketone–Methyl ethyl ketone; 5, Diallyl ether–Di-*n*-propyl ether; 6, Ethyl vinyl ether–Diethyl ether; 7, *n*-Butyl vinyl ether–*n*-Butyl ethyl ether; 8, Tetrahydrofuran–Furan.

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[1] Detailed descriptions on this phenomenon will be given in a subsequent paper.

TABLE 4. π-ELECTRON-MOBILITY INDEXES AND ELECTRONIC PROPERTIES OF VINYL COMPOUNDS

No.	Vinyl compound	I_{em}	λ_{ho}[a] (β)	η_{lv}[a] (β)	q_α[b]	q_β[b]	$\frac{q_\alpha+q_\beta}{2}$[b]	D_π[c] (kcal/mol)	$\sigma_R{}^p$
1	Furan	0.98	—	—	—	—	—	—	—
2	*n*-Butyl vinyl ether	0.55	—	—	—	—	—	—	−0.58
3	Ethyl vinyl ether	0.53	0.354	1.118	—	—	—	—	−0.50
4	Vinyl acetate	0.36	0.850	0.958	1.033	0.931	0.982	58.2	−0.08
5	Acrylonitrile	0.22	0.855	0.407	1.019	0.849	0.934	46.2	0.08
6	Diallyl ether	0.092	—	—	—	—	—	—	—
7	Methyl acrylate	0.053	1.077	0.453	1.037	0.804	0.921	49.3	0.13
8	Ethyl acrylate	−0.03	—	—	—	—	—	—	0.13
9	4-Vinylpyridine	−0.08	—	—	—	—	—	—	—
10	Methyl methacrylate	−0.16	0.845	0.487	—	—	—	40.3	—
11	Acrolein	−0.44	1.161	0.315	1.087	0.685	0.886	48.7	0.15
12	Methyl vinyl ketone	−0.53	1.137	0.448	1.052	0.769	0.910	50.9	0.22

a) λ_{ho} and η_{lv} are the coefficients of the energies of the highest occupied π-level ($\varepsilon_{ho}=\alpha+\lambda_{ho}\beta$) and of the lowest vacant π-level ($\varepsilon_{lv}=\alpha-\eta_{lv}\beta$), respectively. Data in Ref. 11.

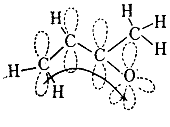
b) q_α and q_β are the π-electron densities of α-carbon and β-carbon in the vinyl compound ($\overset{\beta}{C}H_2=\overset{\alpha}{C}HY$).

c) Data in Ref. 12.

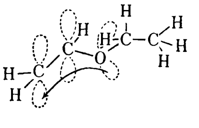
vinyl ketone and methyl ethyl ketone. It may be noted from this comparison that the Φ_A is markedly affected by the substitution of vinyl group for ethyl group bonding with the substituent group Y. In order to clarify the phenomena, we plotted the Φ_A of the vinyl compounds against that of the ethyl compounds, as is shown in Fig. 6; for convenience, we classified them into the following three types: (i) Φ_A(vinyl)$>\Phi_A$(ethyl), (ii) Φ_A(vinyl)$\simeq\Phi_A$(ethyl), and (iii) Φ_A(vinyl)$<\Phi_A$(ethyl). Since the introduction of a hetero atom to the proton-accepting molecule as an unsaturated hydrocarbon molecule results in an enhanced Φ_A, the hydrogen atom in a silanol molecule is considered to form a hydrogen bond more preferentially with the hetero atom than with the vinyl group. Therefore, the difference in the Φ_A values of the vinyl and ethyl compounds with the same substituent should indicate directly the difference in the electronic natures of the hetero atoms in the substituents. In other words, it can be said that the difference in the Φ_A indicated the π-electron drift between the vinyl group and the neighboring hetero atom.

Typical pairs of compounds belonging to the (i) and (iii) types are methyl vinyl ketone–methylethyl ketone and ethyl vinyl ether–diethyl ether respectively:

Methyl vinyl ketone
$\Phi_A(\text{vinyl}) = 112.0\ \text{cm}^{-1}$
$\Phi_A(\text{ethyl}) = 73.0\ \text{cm}^{-1}$



Ethyl vinyl ether
$\Phi_A(\text{vinyl}) = 51.7\ \text{cm}^{-1}$
$\Phi_A(\text{ethyl}) = 108.8\ \text{cm}^{-1}$



In methyl vinyl ketone, it can be considered that the π-electrons of the vinyl group migrate from the vinyl group to the carbonyl oxygen whose lone-pair electrons associate with the hydrogen atom in a silanol molecule, resulting in a lowering of the π-electron density of the vinyl group or in a lowering of the energy level of the π-electrons of the vinyl group. In the case of ethyl vinyl ether, it can be considered that the lone-pair electrons of an oxygen atom which have some π-characteristics transfer to the vinyl group and enhance the energy level of π-electrons of the vinyl group.

On the basis of the above qualitative consideration, we may defined the π-electron-mobility index (I_{em}), which represents the degree of the mobility of π-electrons of the vinyl group, as follows:

$$I_{em} = \frac{\Phi_A(\text{ethyl}) - \Phi_A(\text{vinyl})}{\Phi_A(\text{ethyl})} \tag{4}$$

The I_{em} values are listed in Table 4.

In order to confirm this definition, we examined the relationships between the I_{em} and the other measures representing the energy level of π-electrons of the vinyl group (Table 4). It is obvious from Table 4 that the I_{em} values are in relation to the coefficients (λ_{ho}) of the highest occupied π-levels ($\varepsilon_{ho}=\alpha+\lambda_{ho}\beta$) rather than to those ($\eta_{lv}$) of the lowest vacant π-levels ($\varepsilon_{lv}=\alpha-\eta_{lv}\beta$) of vinyl compounds, as calculated by the method of the simple Hückel MO.[11]

It may also be seen in Table 4 that the I_{em} values are correlated with the average π-electron densities

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[11] T. Kagiya, Y. Sumida and T. Nakata, This Bulletin, **41**, 2239, 2247 (1968).

$(q_\alpha+q_\beta)/2$ of the vinyl groups, where q_α and q_β are, respectively, the π-electron densities of α-carbon and β-carbon; the larger the values of $(q_\alpha+q_\beta)/2$, the larger the I_{em} values. It may be concluded from these results that the I_{em} is a measure not only of the energy level of the highest occupied π-orbital of vinyl compound, but also of the average π-electron density of the vinyl group.

There is, however, no relationship between the I_{em} and the π-bond dissociation energies of the vinyl compounds, which depend upon the electronic nature of the vinyl group.[11,12] This means that the I_{em} indicates the degree of π-electron drift in the molecule, but not essentially the strength of the π-bond.

Moreover, in order to elucidate the resonance effect on the I_{em} values, we then plotted the I_{em} against the substituent constants, $(\sigma_R{}^p)$, due to the resonance effect. As is shown in Fig. 7, there exists a good correlation — the I_{em} becomes larger as the $\sigma_R{}^p$ decreases.

It seems reasonable to conclude from the above correlations that the I_{em} is a semi-quantitative measure of the various electronic properties of π-electrons of the vinyl groups.

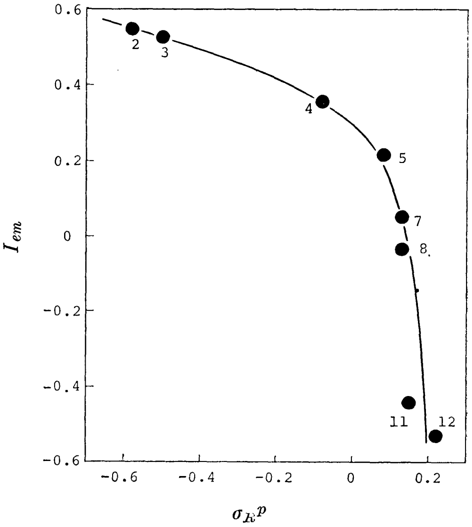

Fig. 7. Relation between the π-electron-mobility indexes I_{em} and the resonance substituent constants $\sigma_R{}^p$. The number of a point represents the number in Table 4.

The authors would like to express their gratitude to Mr. Takeshi Watanabe for his technical assistance.

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[12] T. Kagiya and Y. Sumida, *Polymer J.*, **1**, 137 (1970).