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Intermolecular Hydrogen Bond Involving a π Base as the Proton Acceptor. IX. Hydrogen Bonding of Phenol to Monoolefins

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The π hydrogen bonding between phenol and monoolefins has been studied by examining the OH stretching vibration spectra of phenol in the presence of monoolefins. From comparison of the hydrogen bond shifts, it has been shown that the basicity of the aliphatic olefins toward phenol increases with the increasing alkylsubstitution on the double bond carbon. The endocyclic olefins are more basic than $RCH{=}CH_2$ and $RCH{=}CHR'$ where R and R′ represent alkyl groups. The equilibrium constants for complex formation with olefins were smaller than those with aromatic hydrocarbons. The steric effects on the hydrogen bond complex with aliphatic and endocyclic olefins have been discussed.

In relation to the various proposed conformations of olefin carbonium ions[1] the investigation of the hydrogen bonds involving olefins as the base is of interest, since hydrogen bonding could be the first step of the proton transfer.[2] Several examples are found in literatures.[3-6] The effect of structure (but not of strain) of base upon hydrogen bonding has been studied by West[5] and Kuhn and Bowman.[6] However, the influences of structure and strain of base on the hydrogen bonding have not been studied so far. The present paper describes the infrared data on hydrogen bonding of phenol with straight, branched and cycloolefins. The frequency shifts of the hydroxyl stretching vibration of phenol and the free energy changes due to complex formation were found to be strongly affected by the structure of the olefins. These variations are explained in terms of steric strain and electronic effects.

Experimental

Materials. 1-Olefins were prepared by pyrolysis of the methyl esters of the corresponding alcohols at 470—515°C under nitrogen atmosphere.[7,8] Cyclopentene and cycloheptene were prepared by dehydration[9,10] of the cycloalcohols obtained by hydrogenation[11] of the ketones.[12,13] The other materials were commerical products and purified by the usual methods, special care being taken to remove all traces of water. Their purity was confirmed by gas chromatography, using Apiezon L or β,β'-bispropionitrile ether columns.

Measurements and Analysis of Spectra. Hydroxyl stretching vibration spectra of phenol were recorded on a Double Pass High Precision Spectrophotometer of Japan Spectroscopic Co. A pair of 0.10 cm cells equipped with NaCl windows were used for double path operations. The concentration of olefins were 1—7 mol/*l* and that of phenol 0.01—0.02 mol/*l* in carbon tetrachloride. The detailed conditions for measuring the ν_{OH} spectra of phenol have been described previously.[14] The analysis of the observed spectra was carried out by use of the Lorentz equation[15] as mentioned in previous papers.[14-16] The equilibrium constants were calculated according to a previous paper.[14]

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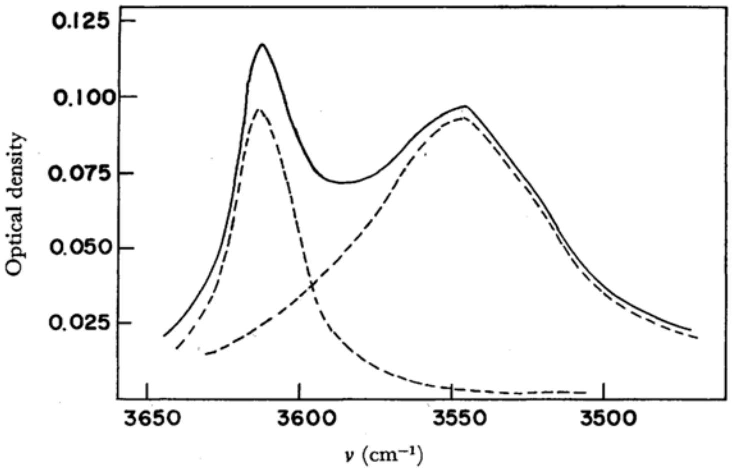

Fig. 1. OH strecthing absorption spectrum of 0.0174M phenol in the presence of 6.97M 1-pentene in CCl_4. Broken lines are analyzed component curves according to the Lorentz equation.

Results and Discussion

The hydroxyl stretching vibration spectra of phenol in the presence of olefins were all doublets as shown in Fig. 1 for the system of phenol-1-pentene. The hydrogen bond shifts, $\Delta\nu$, and the free energy changes for the complex formation, $-\Delta F$, are summarized in Table 1. Generally the half width of the bonded OH band for olefins was larger than that for aromatic hydrocarbons[14] with similar frequency shifts. For example, the hydrogen bond shifts are nearly equal for 1-octene and *m*-xylene, but the half widths of the bonded OH band were 73 cm^{-1} and 39 cm^{-1}, respectively.

From Table 1 it is apparent that for a given type of olefin, such as a monosubstituted ethylene, the hydrogen bond shifts are nearly constant, but they are strongly affected by the number and the position of alkyl groups attached to the double bond carbon, in the order $RCH{=}CH_2(A) < RCH{=}CHR'(B) < {}^{R}_{R'}\!\!>C{=}CH_2(C)$, where R and R′ are alkyl groups. This trend is interpreted in terms of an increase in the electron density of the double bond with an increase in the total inductive effect due to alkyl-substitution as ascertained in the case of phenol-alkylsubstituted benzenes system.[16] Since the frequency shift is a good measure of the base strength of the proton acceptor,[17-19] the result obtained for aliphatic olefins means that alkyl-substitution at the double bond carbon increases its base strength toward the phenolic proton. This order corresponds well with West's results,[5] but the frequency shift (particularly for 1-olefins) in our investigation was about 1—13 cm^{-1} smaller than those of West. The effect of alkyl substitution on the frequency shift is also expected from the ionization potentials of olefins, the ionization potential of branched aliphatic olefins being smaller

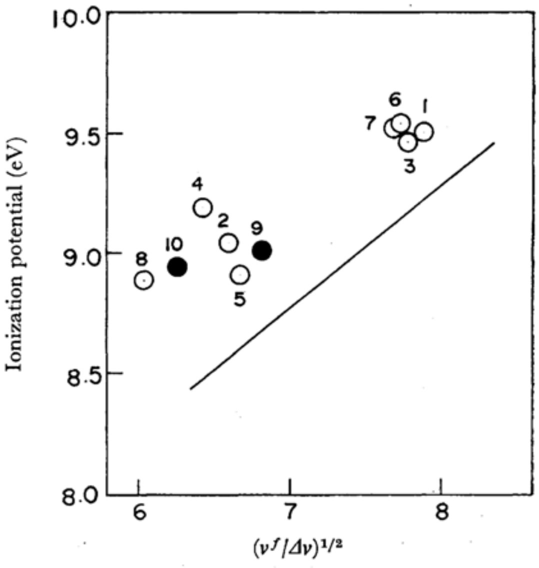

Fig. 2. Correlation between ionization potential of olefins and $(\nu^f/\Delta\nu)^{1/2}$.
○, aliphatic olefins; ●, cycloolefins. The numbers correspond to those listed in Table 1. Solid line is the correlation for phenol-methylbenzenes.

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Table 1. Frequency shifts and change of free energy (29°) in π hydrogen bonding of phenol with monoolefins[f)]

No.	Olefins	$\Delta\nu$ (cm^{-1})	$-\Delta F$ (kcal/mol)	Ionization potential of the proton acceptors (eV)
1	1-Pentene	$58\pm1^{a)}$	$-1.16\pm0.05^{a)}$	$9.50^{b)}$
2	2-Pentene	82 ± 1.5	-1.01 ± 0.07	$9.06^{c)}$
3	1-Hexene	59.5 ± 1	-1.46 ± 0.05	$9.46^{b)}$
4	2-Methyl-1-pentene	87 ± 1	-1.04 ± 0.03	$9.20^{c)}$
5	4-Methyl-2-pentene	81 ± 1.5	-1.03 ± 0.08	$8.89^{c)}$
6	1-Heptene	60 ± 1	-1.37 ± 0.03	$9.54^{c)}$
7	1-Octene	61 ± 1	-1.47 ± 0.02	$9.52^{c)}$
8	2-Ethyl-1-hexene	100 ± 1.5	-0.79 ± 0.05	$8.88^{d)}$
9	Cyclopentene	77.5 ± 1	-1.40 ± 0.07	$9.01^{e)}$
10	Cyclohexene	92 ± 2	-0.93 ± 0.09	$8.945^{b)}$
11	4-Methylcyclohexene	93 ± 1.5	-0.93 ± 0.07	
12	Cycloheptene	87.5 ± 1	-1.05 ± 0.06	
13	*cis*-Cyclooctene	88.5 ± 1	-1.19 ± 0.06	
14	Benzene	49 ± 1	-0.66 ± 0.05	
15	Toluene	58 ± 1	-0.56 ± 0.07	
16	*m*-Xylene	69 ± 1	-0.53 ± 0.04	
17	Mesitylene	78 ± 1	-0.34 ± 0.04	
18	Durene	85 ± 1	-0.31 ± 0.05	
19	Hexamethylbenzene	106 ± 1	-0.28 ± 0.03	

a) Mean deviation from the average.

b) Refs. 20 and 21.

c) J. Collin and F. P. Lossing, *J. Am. Chem. Soc.*, **81**, 2064 (1959).

d) This value was calculated from the relation desribed by Turner (D. W. Turner, "Determination of Organic Structure by Physical Methods," ed. by F. C. Nachod and W. D. Phillips, Vol. 2, Academic Press, New York and London (1962), p. 354).

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f) The data for methyl substituted benzenes were taken from a previous paper (Ref. 14).

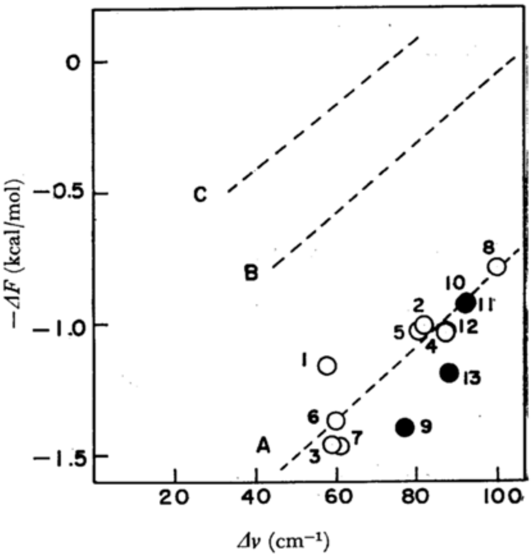

Fig. 3. $-\Delta F$ *vs.* $\Delta\nu$ plot with phenol-olefin complexes. Numbers correspond to those listed in Table 1. ○, aliphatic olefins; ●, cyclic olefins. (A) olefin line, (B) alkylbenzene line, (C) polyacene line.

than those of the linear ones.[20,21] The importance of charge-transfer in hydrogen bond interaction has been suggested by many workers,[22] and it has been demonstrated[19,23] that a linear correlation between the ionization potential of the aromatic donor and $(\nu_f/\Delta\nu)^{1/2}$ is observed. Such correlation was also obtained for phenol and olefins system as shown in Fig. 2.

Table 1 shows that the free energy change, $-\Delta F$, in π hydrogen bond formation increases with the frequency shifts. Accordingly, the more basic the proton acceptor, the easier the complex formation. In contrast, these $-\Delta F$ values are smaller than those obtained for aromatic hydrocarbons as the proton acceptors. For example, while the frequency shifts for mesitylene and 4-methyl-2-pentene are about the same, $-\Delta F$ for the latter (−1.03 kcal/mol) is much (*i. e.* −0.30 kcal/mol) smaller than that for the former. The plot of $-\Delta F$ *vs.* $\Delta\nu$ (Fig. 3) shows that $-\Delta F$ depends strongly on the type of the π base; monoolefins behave as a distinct group from polycondensed aromatics and alkylbenzenes. According to our previous considerations,[14,16] the entropy decrease for the phenol monoolefin interactions is the largest. In charge-transfer complexes involving alkylbenzenes and olefins as the electron donor, however, the formation constants as well as the entropy changes are nearly equal.[24] This suggests that degrees of freedom of movement of the electron acceptor molecule should be much smaller in the case of π hydrogen bond interactions involving

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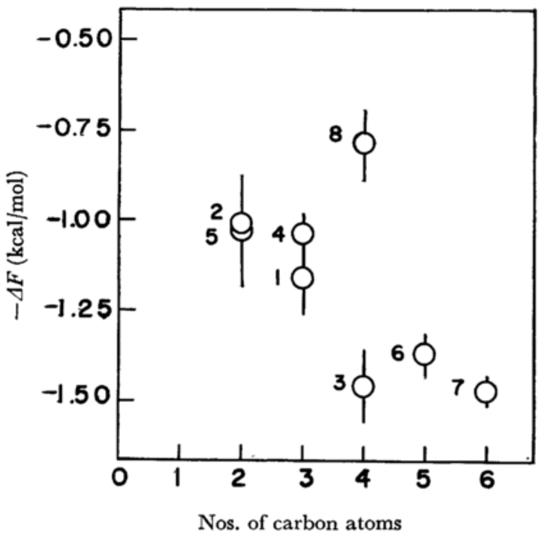

Fig. 4. Dependence of lenght of the carbon chain adjacent to olefinic double bond on $-\Delta F$. Numbers correspond to those listed in Table 1.

olefins as the electron donor than in the case of typical charge-transfer complexes. It can be seen from Table 1 that the increasing length of the alkyl group attached to the double bond carbon causes a decrease of $-\Delta F$. This trend is significant in the α-olefin series, where $-\Delta F$ decreases with the increasing length of the alkyl group while the frequency shifts being nearly constant (See Fig. 4). This could be due to steric hindrance. The steric hindrance has also been observed in the Ag^+-olefin complex formation.[25]

From a comparison of $-\Delta F$ values of the hydrogen bonded complexes with those of the Ag^+-olefin complexes it is shown that the branched olefins give more stable complexes for the hydrogen bond formation, and less stable complexes for the argentation than in the case of α-olefins. This opposite relation of basicity of the alkyl-substituted olefins toward phenolic proton and Ag^+ might be explained in terms of π (for the π hydrogen bonding) and σ complex-formations (for the argentation). If this is correct, the phenolic proton approaches the π electron cloud of olefin along the *z* axis, assuming that the olefin molecule lies on the *xy* plane with the *y* axis passing through the carbon atom of the double bond.[1b] The steric hindrance (Fig. 4) in such configuration of the π hydrogen bond complex could be explained as follows. The carbon chain of the alkyl groups adjacent to the double bond could freely rotate in solution. Since the aliphatic olefins used in this work have *trans*-form, judging from their boiling points, the saturated carbon chain has a considerable rotational freedom around the carbon-carbon single bonds. Accordingly, the length of the alkyl group would control the stability of π hydrogen bonded complex.

Table 2 shows that endocyclic olefins are more basic than RCH=CHR′ where R and R′ are alkyl groups, though the ring size of the endocyclic olefins has an effect on the value of $\Delta\nu$. The decreasing order of $\Delta\nu$ and $-\Delta F$ is the following: cyclohexene>cycloheptene≈*cis*-cyclooctene>cyclopentene. This result differs from the order of the equilibrium constants for Ag^+-complexes involving the endocyclic olefins as the electron donor.[26] If the linear Badger-Bauer relationship[27] between $-\Delta H$ and $\Delta\nu$ is correct, the effects of variations in ring size on $-\Delta F$ may be attributed to differences in ring strain, resulting from deformations and hydrogen-hydrogen repulsion with the endocyclic olefins. If we assume that the steric strain of cycloolefins is correlated with the distortion of the C=C–C bond angle, the differences in $\nu_{C=C}$ for cyclohexene and other cycloolefins will be a measure of the steric strain.[28] Table 2 shows that the smaller the $\Delta\nu_{C=C}$ value, the easier the formation of π hydrogen bond complexes. Namely, in π hydrogen bond ring strain does not appear to lead or facilitate deformation strain of the π orbital for complex formation as observed in the argentation of the cycloolefins.[26] This would suggest that the hydrogen bonded complexes are π complexes, while the Ag^+-complexes would be of the σ type.

TABLE 2. STRETCHING FREQUENCY OF CARBON-CARBON DOUBLE BOND $\nu_{C=C}$ FOR CYCLOOLEFINS, AND CHANGE OF FREE ENERGY IN THE PHENOL-CYCLOOLEFINS SYSTEM

Cycloolefin	$\nu_{C=C}$ a) (cm^{-1})	$\Delta\nu_{C=C}$ (cm^{-1})	$-\Delta F$ (kcal/mol)
Cyclopentene	1611	35	−1.40
Cyclohexene	1646	0	−0.93
Cycloheptene	1651	5	−1.05
Cyclooctene	1673	27	−1.19

a) Ref. 28

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