Hydrogen Bonds between *p*-Chlorophenol and Alkylbenzenes

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Hydrogen bonds between organic hydroxy compounds and aromatic compounds, *i.e.*, the so-called π–H bonds, have been studied by many authors, for example, methyl alcohol - methylated benzene complexes were examined by Krueger and Mettee.[1]

When *p*-chlorophenol was used instead of methyl alcohol, the shift of the OH-stretching frequency was greater than in the case of methyl alcohol. In this case *p*-chlorophenol was used as the proton donor, and methylated, ethylated and isopropylated benzenes were used as proton acceptors.

The OH-stretching frequency shifts, $\Delta\nu$, the enthalpy changes, $-\Delta H$, the entropy changes, $-\Delta S$, and the equilibrium constants, K, for π–H complexes formed in a carbon tetrachloride solution were obtained and compared with other findings on hydrogen-bonded complexes.

Experimental

The infrared absorption spectra were recorded with a Jasco Diffraction Grating Infrared Spectrophotometer, Model DG 201.

The concentrations of *p*-chlorophenol were regulated so as to have an order of magnitude of 0.001 mol/*l* and so as not to form hydrogen bonds among themselves, while those of alkylbenzenes were 0.5 mol/*l*, except for penta- and hexamethylbenzenes, which had a 0.2 mol/*l* concentration because of their low solubilities.

The temperatures of the solutions were altered by 10° stages from 15°C to 74°C in order to obtain $-\Delta H$ and $-\Delta S$ from the change in the absorption intensities of the free and hydrogen-bonded OH-stretching frequencies.

Results and Discussion

The observed values of $\Delta\nu$, $-\Delta H$, $-\Delta S$, and K are listed in Table 1. The frequency shift, $\Delta\nu$, seems to correlate extremely well with the number, n, of alkyl groups and little with their mutual configurations. The correlations are represented by a linear relation, *i.e.*, $\Delta\nu = an + 47$, shown in Fig. 1.

The gradients, a, were 9.0 in methylated benzenes, 7.9 in ethylated benzenes, and 9.7 in isopropylated benzenes, while the standard deviations were 0.3, 0.2, and 0.1 respectively.

The same linear correlation may be found from the table of methyl alcohol - methylated benzene complexes,[1] where a is 8.7 ± 1.7 and where the 47 constant is replaced by 23. It is interesting to see that the gradients are nearly equal to each other irrespective of the species of alkyl groups in the proton acceptors and of the proton donors.

The linear relationship between $\Delta\nu$ and ΔH (Badger-Bauer's rule) does not hold in this study

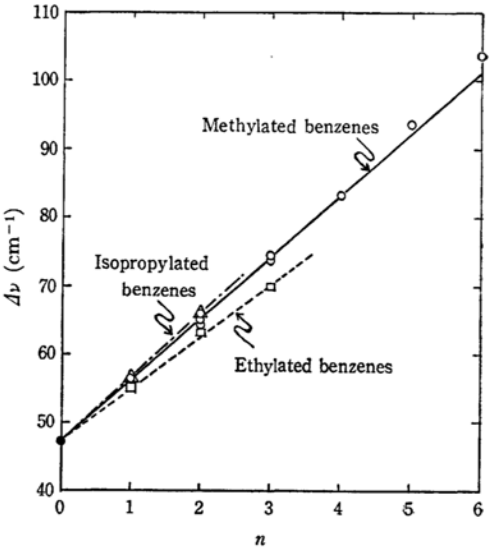

Fig. 1. The correlations between the OH frequency shifts $\Delta\nu$ of *p*-chlorophenol and the number n of alkyl groups in alkylbenzenes.

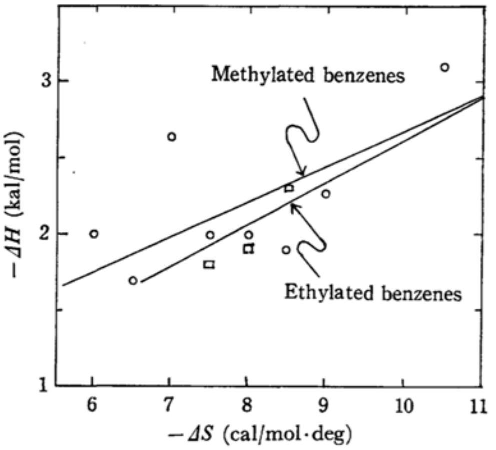

Fig. 2. The correlations between $-\Delta H$ and $-\Delta S$ of *p*-chlorophenol - alkylbenzene complxes.

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[1] P. J. Kruegar and H. D. Mettee, *Can. J. Chem.*, **42**, 288 (1964).

TABLE 1. VALUES OF $\Delta\nu$, $-\Delta H$, $-\Delta S$ AND K OF π-H COMPLEXES OF *p*-CHLOROPHENOL AND PROTON ACCEPTORS

Proton acceptor	$\Delta\nu$ (cm^{-1})	$-\Delta H$ (kcal/mol)	$-\Delta S$ (cal/mol·deg)	K (at 23°C)
Benzene	47	4.4	18	0.21
Toluene	56	1.9	8.5	0.35
o-Xylene	63.5	2.3	9	0.53
m-Xylene	66	2.0	8	0.50
p-Xylene	65	1.7	6.5	0.60
Mesitylene	74	1.7	6.5	0.60
Pseudocumene	73.5	2.0	7.5	0.62
Durene	82.5	3.1	10.5	0.80
Pentamethylbenzene	93.5	2.0	6	1.45
Hexamethylbenzene	103	2.4	7	1.82
Ethylbenzene	55	1.9	8	0.43
Diethylbenzene	62.5	2.3	8.5	0.60
Triethylbenzene	70	1.8	7.5	0.55
Cumene	56.5	2.6	10	0.60
Diisopropylbenzene	66.5	2.8	10.5	0.51
t-Butylbenzene	57.5	1.9	8	0.48

either, as Pimentel and McClellan have pointed out that it does not hold for many other examples of hydrogen-bonded complexes.2)

The ΔH *vs.* ΔS relation seems to be nearly linear, as in many other complexes,1,2) although the deviation from linearity is rather large (Fig. 2). The equilibrium constant, K, tends to increase monotonously as n increases. This trend is quite different from that of the methyl alcohol - methylated benzene series,1) which has shown the minimum value when $n=2$.

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2) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Company, San Francisco and London (1960), p. 85.