

Spectroscopic Investigations on Derivatives of Tetrahydrofuran. II. The Basicity of 2-Substituted Tetrahydrofurans

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IR spectra of some complexes of 2-substituted tetrahydrofurans with phenol in carbon tetrachloride have been measured. $\nu(\text{OH})$ and K_{as} values can be correlated with Taft's σ^* constants. The basicity of 2-substituted tetrahydrofurans under investigation increases proportionally with I-effects of the substituents. No steric effects have been found.

From five-membered ring systems tetrahydrofuran and tetrahydrothiane were chosen by Tanaka [1] for investigation of the effect of the ring size and of the substituent upon the basicity of substituted cyclic ethers. The cited author expressed the dependence of the basicity of the investigated systems as a function of electron effects of the substituents as well as of the ring size by a correlation relation *vs.* σ^* constants. Tetrahydrofuran was, in determination of association constants of complexes of cyclic ethers with phenol, included also by Lippert and Prigge [2]. We tried to apply this principle in the investigation of some other 2-substituted tetrahydrofurans (II–VIII, compare Table 1) because, in agreement with the authors [2], we found that complete complex formation occurs only when the ratio ether–phenol is 1 : 25–50. Our work based on the results of Huggins and Ahlf [3, 4] who found that in phenol solutions there is an equilibrium between the monomer and the trimer of which the former exists until the concentration 0.01 M is reached.

In this study wave numbers of the peaks of absorption bands of complexes of phenol with 2-substituted tetrahydrofurans have been measured. No association of phenol molecules was registered by our instrument until the concentration 0.02.

Based on the presumption that the complex is formed in the ratio 1 : 1 [2] the K_{as} values were calculated from the decrease of absorption of the pure solution of phenol, after addition of 0.1 M solution of ether. According to the equation used by Lippert [2]

$$K_{\text{as}} = \frac{[A^0] - [A]}{[A]([D^0] - [A^0] + [A])} \cdot \frac{F_{20}^0}{F_t^0} = \frac{[AD]}{[A][D]},$$

where $[AD]$, $[A]$ and $[D]$ are the concentrations of H-bonded complex of the acceptor (free phenol) and those of donor of electrons; $[A^0]$ and $[D^0]$ are the initial concentrations of phenol and donor; F_t^0 is integrated absorption intensity of the absorption band corresponding to free OH groups of phenol at temperature t . In our work both the absorption of 0.02 M phenol and of the complex were measured at

Table 1

Equilibrium association constants and integrated absorption intensities of the complexes of phenol with 2-substituted tetrahydrofurans

Compound Substituent	I H	II Me	III Et	IV n-Pr	V Ph	VI CH ₂ Ph	VII CH ₂ Br	VIII CH ₂ CN
σ^*	0.49	0.00	-0.1	-0.115	0.6	1.3	0.225	1.0
$\Delta\nu$ [cm ⁻¹]	282	294	297	300	254	242	280	247
K_{as} [l mole ⁻¹]	6.53	7.71	7.93	8.18	4.75	0.07	—	1.666
	6.51	8.5	—	8.81	—	—	—	—
A_i rel	20.3	30.45	28.6	34.58	17.0	4.72	—	6.116
	20.32	30.4	—	30.93	—	—	—	—

$\Delta\nu = \nu_0 - \nu$, where ν_0 is the wave number of the absorption band of hydrogen bonded OH groups and ν is the wave number of the free OH group of phenol.

σ^* values are taken from ref. [10].

$35 \pm 2^\circ\text{C}$ and thus the expression F_{20}^0/F_t^0 cancels out. K_{as} value found for tetrahydrofuran is in good agreement with the one found by Lippert and Prigge [2] ($7.53_{30^\circ\text{C}}$; $5.94_{40^\circ\text{C}}$).

The order of K_{as} was checked also by determination of the ratio of integrated absorption intensities (A_i rel) of the complex and that of phenol.

In order to ascertain whether the increase in basicity of 2-substituted tetrahydrofurans is proportional to the I-effect of the substituents or if steric effects also contribute to it all, the calculated as well as the found values ($\Delta\nu(\text{OH}\dots\text{O})$, K_{as} , A_i rel) were compared both with Taft's polar substitution constants σ^* and the constants E_s . The results are summarized in Table 1 and pictured on Figs. 1–3. Good correlation was also found between the values $\Delta\nu(\text{OH})$ and $\text{p}K_b$ calculated according to Tanaka's equation [1]

$$(\text{p}K_b)_{mi} = b_m \sum_i \sigma^* + (\text{p}K_b)_{m 2(\text{CH}_3)},$$

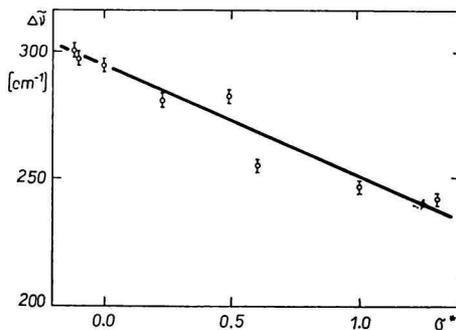


Fig. 1. Wave numbers of the complexes of phenol with 2-substituted tetrahydrofurans vs. Taft's polar substitution constants of the substituents.

The least-square method gave for $y = (293.74 \pm 3.416) - (43.52 \pm 5.27) x$.

Anderson's correlation coefficient $r = 0.95699$.

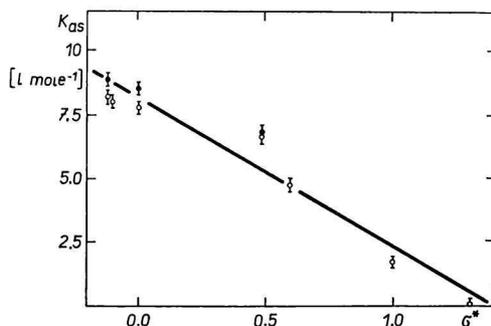


Fig. 2. Equilibrium association constants of the complexes of phenol with 2-substituted tetrahydrofurans vs. Taft's polar substitution constants of the substituents.

$$y = (8.04 \pm 0.35) - (5.69 \pm 0.56) x.$$

$$\text{Correlation coefficient } r = -0.9746.$$

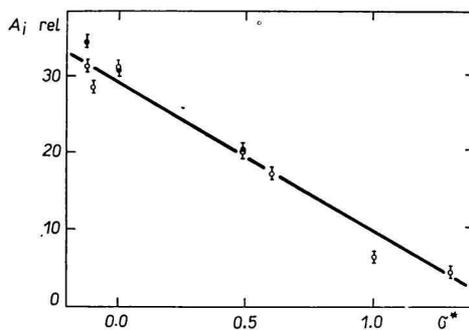


Fig. 3. Ratio of integral absorptions of the complexes of phenol with 2-substituted tetrahydrofurans and that of free phenol (A_i rel) vs. Taft's polar substitution constants of the substituents.

$$y = (29.502 \pm 0.892) - (20.405 \pm 1.42) x.$$

$$\text{Correlation coefficient } r = -0.9913.$$

The total error due to the error of reading of the absorption is 2%.

Table 2

Correlation of $(pK_b)_i$ values from Tanaka's equation [1] with σ^* values

Compound Substituent	I H	II Me	III Et	IV <i>n</i> -Pr	V Ph	VI CH ₂ Ph	VII CH ₂ Br	VIII CH ₂ CN
$\Sigma \sigma^*$	0.98	0.49	0.39	0.375	1.09	0.705	1.49	1.76
pK_b	4.97	4.59	4.51	4.50	5.06	4.76	5.38	5.62

For σ^* and $\Delta\nu$ see Table 1.

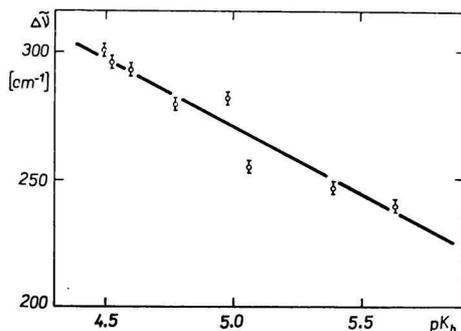


Fig. 4. Values pK_b calculated from Tanaka's equation [1] vs. $\Delta\nu = (545.99 \pm 31.0) - (54.8 \pm 6.8) pK_b$.
Correlation coefficient $r = -0.963$.

where b for a five-membered ring ($m = 5$; $i \sim$ substituents R and H in position 2) is 0.792 and $(pK_b)_{5, 2(\text{CH}_2)} = 4.2$ (Fig. 4, Table 2).

The basicity of the investigated 2-substituted tetrahydrofurans is proportional to the I-effect of the substituents. Steric effects have not been found (correlation of the constants E_s with the values obtained from IR spectra was not satisfactory).

Experimental

IR spectra were run independently on two UR-10 spectrometers (Zeiss, Jena) at $35 \pm 2^\circ\text{C}$. Reading accuracy of wave numbers in the case of broad absorption peaks was $\pm 5 \text{ cm}^{-1}$. Reading accuracy of absorption was $\pm 1\%$. The wave numbers were calibrated against a polystyrene foil. The correlation straight lines were calculated by the least-square method [14] and the correlation coefficient of Anderson's test [11] was determined. The ratio ether—phenol was 25 : 1. The ratio of integrated absorption intensities (A_1 rel) was determined by cutting out the peaks corresponding to the complex and phenol and weighing them.

Tetrahydrofuran (I) was dried over sodium hydroxide pellets and distilled successively in the presence of sodium metal, lithium aluminium hydride and potassium permanganate; b.p. 66.5°C , n_D^{20} 1.4075.

Compounds II, III, IV, V, and VIII were synthesized from 2-chlorotetrahydrofuran and corresponding alkyl magnesium iodide. The purity of rectified products was checked by gas chromatography. Compound II: b.p. $81-82^\circ\text{C}$, n_D^{20} 1.4161 (ref. [12] — b.p. $80^\circ\text{C}/761$ Torr, n_D^{20} 1.4059); III: b.p. $105-106^\circ\text{C}$, n_D^{20} 1.4182 (ref. [5] — b.p. $108^\circ\text{C}/758$ Torr); IV: b.p. $130-131^\circ\text{C}$, n_D^{20} 1.4273 (ref. [5] — b.p. $135^\circ\text{C}/773$ Torr); V: b.p. $105-108^\circ\text{C}/17$ Torr, n_D^{20} 1.5295 (ref. [6] — b.p. $104-108^\circ\text{C}/18$ Torr); VIII: b.p. $110-115^\circ\text{C}/12$ Torr [7].

Compound VII was synthesized from tetrahydrofurfuryl alcohol and phosphorus tribromide [9]. B.p. $61-62^\circ\text{C}/13$ Torr, n_D^{20} 1.4840 (ref. [13] b.p. $61-63^\circ\text{C}/13$ Torr; n_D^{20} 1.4850).

Compound VI was synthesized from 2-bromomethyltetrahydrofuran and potassium cyanide [8]. B.p. $92.4^\circ\text{C}/13$ Torr, n_D^{20} 1.4450 (ref. [8]).

Carbon tetrachloride used was a commercial product dried over calcium chloride and distilled.

Phenol used was a commercial product distilled under nitrogen.

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