

# INFRARED STUDY OF ASSOCIATION EQUILIBRIA BETWEEN MONOSUBSTITUTED PHENOLS AND VALERONITRILE: INTENSITY MEASUREMENTS

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Received September 27th, 1971

Integral intensities of infrared absorption bands of the  $\nu(\text{OH})$  vibrations were determined in eight binary mixtures monosubstituted phenol-tetrachloromethane and in the corresponding ternary mixtures monosubstituted phenol-valeronitrile-tetrachloromethane. Correlations of the intensities and their logarithms with Hammett substituent constants were found. Validity of the Iogansen relation between the intensities and the standard reaction heat of the hydrogen bond formation was verified for the phenol-valeronitrile complexes.

At present infrared spectroscopy utilizes not only the data of spectral band positions, but in an increasing extent also those of band intensities. Relations between the band intensities and intrinsic molecular properties were studied<sup>1-3</sup> and the intensities of the characteristic bands of various compounds obtained experimentally<sup>4</sup>. The intensity studies are interesting especially in the case of compounds forming hydrogen bridges. The formation of hydrogen bond appears markedly particularly in the region of the stretching vibration of the X—H group of the proton-donor — not only by the frequency shift, but also by a manyfold increase of the band intensity. According to some authors<sup>5</sup> the latter is a more characteristic and specific manifestation of the hydrogen bonding than the former.

In the paper<sup>6</sup> the association constants and standard reaction heats were studied for the formation of the hydrogen bond between monosubstituted phenols and valeronitrile. In the paper presented, those data are used for the calculation of the integral intensities of bands corresponding to the stretching vibration of the OH group of phenols in complexes. In addition, the data are supplemented by the intensities of these bands for free phenols (in tetrachloromethane solutions) and the thermodynamic quantities of ethyl ester of *p*-hydroxybenzoic acid.

## EXPERIMENTAL

For the chemicals used see<sup>6</sup>. Ethyl ester of *p*-hydroxybenzoic acid has been obtained in the Laboratory of monosaccharides, Institute of Chemical Technology, Prague. The spectra were scanned on the grating infrared spectrophotometer Perkin-Elmer 325 (Bodenseewerk Perkin-Elmer, FRG) using spectral slit width  $1.3 \text{ cm}^{-1}$ . A variable path length cell was used in the range of 0.8–6.0 mm for measuring the integral intensities of the bands of free phenols. The band inten-

sities of phenols bound in complexes were measured in a fused quartz cell 10 mm thick, placed in a water-thermostated block. The temperature of the solution in the cell was measured by a copper-constantan thermocouple and kept at the value  $30 \pm 0.1^\circ\text{C}$  by means of the ultrathermostat U 10 (Prüfgeräte-Werk Medingen, GDR). The integral intensities were measured by a Reiss planimeter. Solutions  $3.5-4 \cdot 10^{-3} \text{ mol l}^{-1}$  in tetrachloromethane were prepared for the determination of band intensities of free phenols. During the measurements of the band intensities of phenols in complexes, the phenol concentrations were kept within the range of  $3-6 \cdot 10^{-3} \text{ mol l}^{-1}$ ; the bands of the free phenol fractions were eliminated by using the compensation method<sup>6</sup>.

## RESULTS AND DISCUSSION

The series of the phenols studied was chosen so that it covered uniformly the scale of the electronic effect expressed through the Hammett  $\sigma$  constants. Therefore *p*-phenylphenol used in<sup>6</sup> was substituted by ethyl ester of *p*-hydroxybenzoic acid ( $\sigma$  0.52); among alkylphenols only tert-butylphenol was studied. When the intensity changes on the formation of complexes of these phenols with valeronitrile are to be studied, the intensities of the bands of free phenols must be known. It is difficult, however, to compare the data given by different authors using different measurement and evaluation techniques; we have therefore measured also the intensities of these bands.

TABLE I

Integral Intensities ( $A$ ,  $10^3 \text{ l mol}^{-1} \text{ cm}^{-2}$ ,  $\log_{10}$ ) of the  $\nu(\text{OH})$  Band of Monosubstituted Phenols in Tetrachloromethane, Determined by the Tangent Method (1) and the Baseline Method (2). Phenol Concentrations  $3-4 \cdot 10^{-3} \text{ mol l}^{-1}$

Half band widths determined at the cell thickness 5 mm.

Substituent	$\nu_{\text{max}}$ $\text{cm}^{-1}$	$\Delta\nu_{1/2}^a$ $\text{cm}^{-1}$	Intensity				
			(1)	(2)	lit.		
H	3 612	17.2	4.98	5.77	4.28 <sup>8</sup> , 5.2 <sup>17</sup> , 6.33 <sup>23</sup>	5.06 <sup>11</sup> , 4.31 <sup>21</sup> , 5.2 <sup>24</sup>	5.0 and 4.99 <sup>22</sup> , 5.06 <sup>25</sup>
<i>p</i> -(CH <sub>3</sub> ) <sub>3</sub> C	3 613	16.0	4.77	5.55	4.61 <sup>21</sup>	—	—
<i>p</i> -F	3 614	17.3	5.39	6.25	—	—	—
<i>p</i> -Cl	3 610	19.0	5.52	6.42	5.42 <sup>8</sup> , 6.34 <sup>22</sup>	5.76 <sup>11</sup> , 6.67 <sup>23</sup>	5.17 <sup>21</sup> ,
<i>p</i> -Br	3 609	19.4	5.45	6.33	5.39 <sup>8</sup>	5.34 <sup>21</sup>	6.30 <sup>22</sup>
<i>m</i> -Cl	3 607	20.4	6.10	7.10	5.85 <sup>11</sup>	5.69 <sup>21</sup>	6.52 <sup>22</sup>
<i>p</i> -COOC <sub>2</sub> H <sub>5</sub>	3 603	19.9	6.12	7.13	—	—	—
<i>m</i> -NO <sub>2</sub>	3.602	23.0	6.75	7.83	7.6 <sup>11</sup> , 7.43 <sup>19</sup>	10.5 <sup>20</sup>	—

The values of intensities given in papers<sup>8,21,22,24</sup> in natural logarithms are multiplied by 0.434, those given in papers<sup>11,23,25</sup> in absolute units are multiplied by  $8.73 \cdot 10^9$ . The value  $I$  in<sup>17</sup> is multiplied by  $0.434 \cdot 3611 = 1.57 \cdot 10^3$ .

In order to eliminate the effect of finite slit width, the Wilson-Wells method<sup>7</sup> was applied for the determination of the true intensities. A constant concentration and variable cell thickness was used to eliminate the concentration effects, particularly the self-association of phenol. The spectra showed that the baseline, obtained by measuring the spectrum of neat tetrachloromethane compensated by the same solvent in the reference cell of the same thickness, represents a line which does not touch the spectral curve of phenol even in wide wavenumber limits. Flynn and coworkers<sup>8</sup>, who obtained the same results, assume that the true intensity values can be determined by integrating the area not above this baseline, but above a straight line representing the tangent of the two band wings. In fact, by comparing the spectra of a series of aliphatic alcohols they arrived at the conclusion that the difference of the two areas is due to the remainder of the molecule. Our measurements showed that the area difference for the two techniques makes about 12–20% (when including the Ramsay wing correction during the integration above the baseline).

The results obtained in the two ways as well as the literature data are summarized in Table I. As it can be seen, our data agree well with the literature values; our value for *m*-nitrophenol is slightly lower than the literature value, it correlates, however, better with the Hammett constants. The values obtained by integrating above the tangent were utilized in further correlations. Fig. 1 shows the dependence of the intensities (*A*), their logarithms and square roots on the Hammett constants. In the given range and with the given scatter of the values, linear correlation is obviously

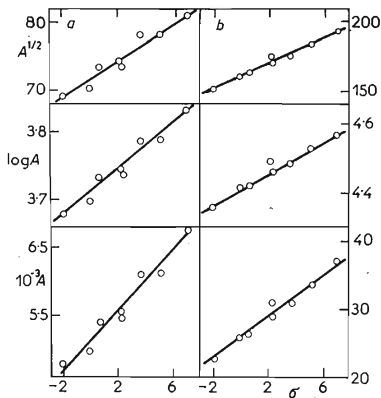


FIG. 1

Functions of Integral Intensities (*A*) in Dependence on the Hammett Constants for the  $\nu(\text{OH})$  Band of Monosubstituted Phenols

*a* Free phenols in tetrachloromethane; *b* phenols bound in complexes with valeronitrile in tetrachloromethane.

equally justified for the three cases. The correlation of the  $\log A$  values is the most usual<sup>9</sup>; the correlation of the  $A^{1/2}$  values has a theoretical background, as shown by Brown<sup>10</sup>. Rao and Venkataraghavan<sup>9</sup> evaluated statistically the values measured by Stone and Thompson<sup>11</sup> and obtained the relation

$$\log A' = 0.790 + 0.137\sigma.$$

The comparison with the original paper by Stone and Thompson indicates, however, that the authors of <sup>9</sup> have dealt with the original values of  $A'$  expressed in absolute units ( $\text{cm}^2 \text{s}^{-1} \text{mol}^{-1}$ ), but that they omitted the characteristics  $-7$ . When recalculating the data according to the relation  $\log A = \log A' + 9.941$  we obtain

$$\log A = 3.731 + 0.137,$$

which approaches the expression derived from our values (Table I, Fig. 1a)

$$\log A = 3.709 + 0.166.$$

The substituents used in<sup>11</sup> cover a wider range of  $\sigma$  values as compared with our series; on the other hand, the scatter of the values correlated<sup>11</sup> is so high that no accurate agreement with any other work can be expected. The comparison of the intensities by the direct integration with those calculated by using the Ramsay approximation<sup>12</sup> leads to the value of the Ramsay constant  $K \approx 1.2$ , similar to the result of Stone and Thompson. Further the intensities of the absorption band of the OH group of phenols bound in complexes with valeronitrile were determined.

With the concentrations used, valeronitrile has a relatively high nonspecific absorption in the region studied. Therefore the spectrum of the solution of valeronitrile in tetrachloromethane (with

TABLE II

Positions, Half Band widths ( $\text{cm}^{-1}$ ), and Integral Intensities ( $A$ ,  $10^3 \text{ l mol}^{-1} \text{ cm}^{-2}$ ,  $\log_{10}$ ) of the  $\nu(\text{OH})$  Bands on Monosubstituted Phenols Bound in Complexes with Valeronitrile

Concentrations: phenols  $\sim 5 \cdot 10^{-3} \text{ mol l}^{-1}$ , valeronitrile variable up to  $0.3 \text{ mol l}^{-1}$ ; the values were obtained by extrapolating to zero concentration of valeronitrile.

Substituent	$\nu_{\text{max}}$	$\Delta\nu_{1/2}$	$A$	Substituent	$\nu_{\text{max}}$	$\Delta\nu_{1/2}$	$A$
H	3 451	104	25.9	<i>p</i> -Br	3 430.5	96	28.8
<i>p</i> -( $\text{CH}_3$ ) <sub>3</sub> C	3 457	102	22.5	<i>m</i> -Cl	3 423	98	30.5
<i>p</i> -F	3 447	98	26.1	<i>p</i> -COOC <sub>2</sub> H <sub>5</sub>	3 410	110	33.3
<i>p</i> -Cl	3 432.5	97	30.6	<i>m</i> -NO <sub>2</sub>	3 390	105	37.0

the neat solvent in the reference cell) was used as the baseline for the measurements using the compensation method (system phenol–valeronitrile–tetrachloromethane in the sample cell, phenol in tetrachloromethane in the reference cell). The spectral curve of the ternary mixture coincides with that of the valeronitrile solution at  $3660\text{ cm}^{-1}$ ; on the low-frequency side, however, a low residual absorption remains. This should be probably attributed to the overlap with the complex band of the CH bond system of phenol in the range of  $3000\text{--}3100\text{ cm}^{-1}$ . We estimate the contribution of this residual absorption to the obtained integral intensity to 5–7%. The finite slit width — regarding the high half band width — has no apparent effect on the intensity values; therefore the results were not treated by the Wilson–Wells method. On the other hand, dependence of the intensities on the concentration of valeronitrile was observed — the intensity increases slightly with the concentration. A similar dependence was also observed for the association constants<sup>13</sup> when the nitrile concentrations higher than  $0.2\text{ mol l}^{-1}$  were applied. The position of the band maximum is also shifted to lower wavenumbers with increasing concentration of the nitrile —  $3\text{--}5\text{ cm}^{-1}$  in the concentration range used (c. up to  $0.3\text{ mol l}^{-1}$ ). This effect had been studied thoroughly in relation to solvent-effects<sup>14,15</sup>. The spectral values listed in Table II are extrapolated to zero concentration of valeronitrile.

A satisfactory correlation of the functions of intensity with the Hammett constants can be seen from Fig. 1b. The logarithm function can be written in the form  $\log A = 4.411 + 0.214\sigma$ . As shown by Iogansen<sup>16</sup>, the intensities are related to the standard reaction heats of the hydrogen bond formation through  $-\Delta H = 0.053 \Delta\Gamma^{1/2}$ , where  $\Delta\Gamma^{1/2} = \Gamma_{\text{bond}}^{1/2} - \Gamma_{\text{free}}^{1/2}$ . Here  $\Gamma = 2.303A/\nu_{\text{max}}$ , where  $\nu_{\text{max}}$  is the wavenumber of the absorption band maximum; the subscripts free and bond refer to the band of the free OH group and that of the OH group bonded by the hydrogen bonding, resp. In the relation mentioned,  $-\Delta H$  is expressed in  $\text{kcal mol}^{-1}$ ,  $\Gamma$  in  $\text{cm}^2\text{ mol}^{-1}$ . Iogansen tested this rule on a variety of systems<sup>17,18</sup> and came to the conclusion that it is more exactly and generally valid than the well-known Badger–Bauer rule<sup>19</sup>. The quantities proving the Iogansen rule are given in Table III. The average value of the

TABLE III

Values of the Iogansen Coefficient of the Relation between the Integral Intensities ( $\Gamma$ ,  $\text{cm}^2\text{ mol}^{-1}$ ,  $\log_e$ ) of the  $\nu(\text{OH})$  Bands of Complexes of Monosubstituted Phenols with Valeronitrile in Tetrachloromethane and the  $-\Delta H$  Values ( $\text{kcal mol}^{-1}$ ) of the Complex Formation

Substituent	$\Gamma_{\text{free}}^{1/2}$	$\Gamma_{\text{bond}}^{1/2}$	$\Delta\Gamma^{1/2}$	$-\Delta H$	$(-\Delta H/\Delta\Gamma^{1/2}) \cdot 10^2$
H	56.3	130.7	74.4	3.99	5.37
<i>p</i> -(CH <sub>3</sub> ) <sub>3</sub> C	55.1	122.4	67.3	3.37	5.01
<i>p</i> -F	58.6	132.0	73.4	4.40	6.00
<i>p</i> -Cl	59.3	143.3	84.0	4.20	5.00
<i>p</i> -Br	59.0	139.0	80.0	4.24	5.40
<i>m</i> -Cl	62.4	143.2	80.8	4.54	5.62
<i>p</i> -COOC <sub>2</sub> H <sub>5</sub>	62.5	150.0	87.5	4.58	5.23
<i>m</i> -NO <sub>2</sub>	65.7	158.5	92.8	6.07	6.54

ratio  $-\Delta H/\Delta T^{1/2}$  is 0.0534, which agrees very well with the rule (the value for *m*-nitrophenol differing considerably from the others was left out); on the other hand, a high scatter of the values for the individual phenols around this average is apparent. In order to enable ethyl ester of *p*-hydroxybenzoic acid to be included, it was necessary to measure its association constant in dependence on temperature by means of the technique described in<sup>6</sup>. With the concentration of the proton-donor  $3.9 \cdot 10^{-3} \text{ mol l}^{-1}$  and that of valeronitrile  $7.25 \cdot 10^{-2} \text{ mol l}^{-1}$  the association constant  $K_{30} 14.1 \text{ l mol}^{-1}$  and standard reaction heat  $-\Delta H 4.58 \text{ kcal mol}^{-1}$  were obtained. The value of the association constant is much lower than would correspond to the Hammett constant according to the correlation derived in paper<sup>6</sup>; a similar result was arrived at by Heinen<sup>20</sup> during his investigation of complexes of phenols with acetone.

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Translated by P. Adámek.