IR STUDY OF ASSOCIATION EQUILIBRIA IN FORMATION
OF COMPLEXES BETWEEN MONOSUBSTITUTED
PHENOLS AND VALERONITRILE

P.Adámek, P.Endrle* and Z.Ksandr

*Department of Analytical Chemistry,
Institute of Chemical Technology, Prague 6*

Hydrogen bonding as a special kind of chemical bond has attracted much attention[1]. In spite of many attempts, there is no unified theory covering this subject. Since the work of Kempter and Mecke[2] phenol has been frequently used as a model proton donor for a study of self-association equilibria or formation of donor–acceptor complexes (cf.[3,4]).

The aim of this work was to get further experimental data on formation of the association complexes between p- or m-substituted phenols as typical proton donors and valeronitrile as the acceptor. In contradistinction to acetonitrile, the complexes of which have been extensively studied, the aliphatic chain of valeronitrile is relatively long, so that data obtained with this nitrile could have a more general validity for comparison with other nitriles.

EXPERIMENTAL

Chemicals

Monosubstituted phenols were chromatographically pure. Valeronitrile was prepared by a reaction of tert-butyl chloride with sodium cyanide[5]. Tetrachloromethane (analytical purity grade, Lachema, Brno) was rectified before use and stored over a molecular sieve.

Method Used

The association equilibria were studied by IR spectroscopy in the region of the fundamental stretching OH vibration. Data for calculation of equilibrium constants were obtained by a compensation method. In the measuring cell was placed the ternary system substituted phenol–valeronitrile–tetrachloromethane, the reference cell was filled with a solution of the phenol in tetrachloromethane. Concentration of the proton donor was chosen so that the free OH absorption band at $\sim 3\,600\ cm^{-1}$ was just compensated. In such a case the association constant in diluted solutions is given by the expression

$$K = (c_D^0 - c_D)/[c_D(c_A^0 - c_D^0 + c_D)]\,, \qquad (1)$$

where c_D^0, c_D^0 are the analytical concentrations of the donor and the acceptor, respectively, and c_D is the analytical concentration of the donor in the reference cell, which should equal to equilibrium concentration of free donor molecules in the ternary system.

To determine association constants we used the following procedure: concentration of the phenol in the reference cell was chosen so that the absorption band of free OH groups in the measuring

*   Present address: Research Institute, Chemické závody českoslov.-sov. přátelství, Záluží u Mostu.

cell was little overcompensated. Then the temperature of the cells was gradually increased until the absorption band of free OH groups was just compensated. By this way the temperature was determined at which the system is governed by the association constant chosen through the known concentrations c_D^0, c_A^0 and c_D. These measurements were carried out with a set of concentrations c_D in order to obtain the association constants K for several different temperatures, from which we interpolated the value of K for 30°C and determined the standard heat of the reaction $-\Delta H$. We made correction for the change in concentrations of the reactants due to change in the density of the solvent with temperature, using the relation[6]

$$\varrho(CCl_4) = 1.63255 - 1.9110 \cdot 10^{-3}t - 0.69 \cdot 10^{-6}t^2$$

The measurements were carried out on a UR 10 spectrophotometer (Zeiss, Jena). In order to prevent self-association of the phenol, we used the donor in concentration about $4-5 \cdot 10^{-3}$ mol/l. For these low concentrations we made a heated cell (1 cm thick) in the following way. NaCl windows were separated by a brassy ring provided with a tapped hole for a thermocouple and with a filling port. That part of the ring which was in contact with the measured solution was covered with a teflon foil. The ring was connected with the windows by means of amalgamated leady distance foils. The copper-constantan thermocouple was inserted into the cell in such a way as to prevent its warming-up by infrared radiation, and thus to ensure that it measures correctly the temperature of the solution. The cell was heated from both sides by means of brassy plates with inserted teflon plate provided with resistance wire. The resistance of the wire in each of both plates was 35 ohm. At series connexion of both plates of the measuring and of the reference cell, the voltage of $13-35$ V was necessary for warming-up the solution to $35-50°C$.

TABLE I

Relationship between Association Constant of the System Phenol–Valeronitrile in Tetrachloromethane and Temperature; c_D^0 $5 \cdot 10^{-3}$ mol/l

For the meaning of symbols see text.

c_A^0 10^{-3} mol l^{-1}	c_D 10^{-3} mol l^{-1}	t_1 °C	t_2 °C	t °C	$1/\bar{T}$ 10^{-3} grad^{-1}	K l mol^{-1}	$\log K$	$\log K_t{}^a$
0·1807	2·325	24·5	26·0	25·3	3·350	6·47	0·811	0·812
0·1802	2·400	26·5	28·0	27·3	3·328	6·11	0·786	0·788
0·1803	2·450	26·5	28·5	27·5	3·326	5·87	0·768	0·770
0·1803	2·500	29·0	32·0	30·5	3·293	5·62	0·750	0·754
0·1808	2·575	32·0	34·0	33·0	3·266	5·28	0·723	0·728
0·1802	2·600	35·0	37·0	36·0	3·234	5·19	0·716	0·722
0·1804	2·650	34·5	36·0	35·5	3·239	4·98	0·697	0·704
0·1805	2·700	37·0	39·0	38·0	3·213	4·78	0·679	0·687
0·1808	2·750	39·0	41·0	40·0	3·193	4·58	0·661	0·670
0·1804	2·850	43·0	45·0	44·0	3·153	4·23	0·626	0·637
0·1801	2·950	45·5	49·5	47·5	3·118	3·90	0·591	0·604
0·1804	2·975	48·0	50·0	49·0	3·106	3·82	0·582	0·596

a After correction for volume changes of the solvent.

Table II

Characteristic Quantities for Hydrogen Bond Formation between Substituted Phenols of the Type XC_6H_4OH and Valeronitrile in Tetrachloromethane

Phenol concentrations $4—5 . 10^{-3}$ mol l^{-1}, valeronitrile concentration approx. 0.2 mol l^{-1}.

X	$\log K_{30}$	K_{30} l mol^{-1}	$-\Delta H$ kcal mol^{-1}	$\Delta \nu$ cm^{-1}	σ (ref.[8])
H	0.761 ± 0.008	5.77 ± 0.11	3.99 ± 0.14	161	0.000
p-CH_3	0.674 ± 0.007	4.72 ± 0.08	3.98 ± 0.16		-0.170
p-CH_5	0.646 ± 0.009	4.42 ± 0.09	3.77 ± 0.20		-0.151
p-C_3H_7	0.646 ± 0.005	4.42 ± 0.05	4.06 ± 0.11		. . .
p-iso-C_3H_7	0.660 ± 0.009	4.57 ± 0.09	3.87 ± 0.16	$152—4$	-0.151
p-tert-C_4H_9	0.647 ± 0.006	4.44 ± 0.07	3.37 ± 0.11		-0.197
p-C_8H_{17}	0.647 ± 0.007	4.44 ± 0.07	3.29 ± 0.11		. . .
m-CH_3	0.659 ± 0.005	4.56 ± 0.05	3.05 ± 0.12		-0.069
m-C_2H_5	0.652 ± 0.006	4.48 ± 0.06	3.32 ± 0.11		-0.070
p-C_6H_5	0.800 ± 0.005	6.31 ± 0.07	3.82 ± 0.10	165	0.009
p-F	0.924 ± 0.006	8.40 ± 0.11	4.40 ± 0.16	167	0.062
p-Cl	1.036 ± 0.006	10.87 ± 0.15	4.20 ± 0.16	177	0.227
p-Br	1.056 ± 0.006	11.38 ± 0.16	4.24 ± 0.15	178	0.232
m-Cl	1.103 ± 0.008	12.70 ± 0.23	4.54 ± 0.22	184	0.373
m-NO_2	1.551 ± 0.006	35.6 ± 0.5	6.07 ± 0.20	211	0.710

RESULTS AND DISCUSSION

Results of the measurements are given in Table I. On raising temperature of the cells, the intensity of the negative absorption band of the free OH groups of phenol in the reference cell gradually decreases till at the temperature t_1 the overcompensation cease to be apparent. At the temperature t_2 the absorption band of phenol OH groups in the measuring cell becomes apparent. The temper-
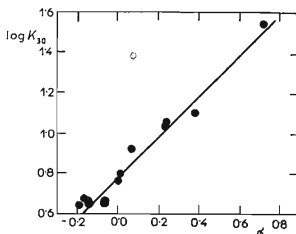

Fig. 1

Relationship between Association Constant of the System Substituted Phenol Valeronitrile in Tetrachloromethane and the Hammett Substituent Constant

ature $\bar{t} = (1/2)(t_1 + t_2)$ was taken as corresponding to the given association constant. The plot $\log K$ versus $1/\bar{T}$ ($\bar{T}$ is $\bar{t}$ expressed in Kelvin degrees) is linear, as expected on the basis of thermodynamic considerations. From the dependences shown in Table I we determined the relations $\log K_t = = p/1$ $(\bar{T}) - q$ and calculated[7] standard deviations from the regression line, s, and regression coefficients, s_p. In Table II are presented the values of $\log K_{30} = 3 \cdot 2988 \cdot 10^{-3} p - q \pm s$ and the reaction heat $- \Delta H = 4 \cdot 575 \cdot 10^{-3}$ $(p \pm s_p)$ (given in kcal/mol; numerical factor includes the gas constant and the factor $2 \cdot 303$ for conversion of logarithms).

Effects of substituents upon equilibrium and rate constants are frequently expressed by Hammett σ constants[8] or by their modifications[9,10]. As it is seen from Fig. 1 the association constants correlate well with σ (Eq. (2)). No significant relationship has been found, however, with the so-called "dual constants", which are frequently employed in correlations of the reactivity and equilibria of phenols. It is worthy of note that a similar correlation has been reported by Heinen[11] in a study of the association of phenols with acetone (Eq. (3)). Both dependences have nearly the same slope, which shows that the association constants for these types of complexes are

$$\log K_{30} = 0 \cdot 79 + 1 \cdot 0\sigma, \tag{2}$$

$$\log K_{23} = 1 \cdot 15 + 0 \cdot 93\sigma \tag{3}$$

nearly directly proportional.

As it is known[1,12], direct proportionality between the frequency shifts $\Delta\nu = \nu_{OH}(\text{donor}) - - \nu_{OH}(\text{complex})$ and the standard heat of reaction $- \Delta H$ is frequently observed when a series of proton acceptors is used for one proton donor. This is not generally true when the formation of association equilibria is studied by using one proton acceptor and a series of proton donors. The change in the $- \Delta H$ values obtained in our case (Table II) is however too small to allow any unambiguous interpretation. On the other hand, the values of $\log K$ can be linearly correlated
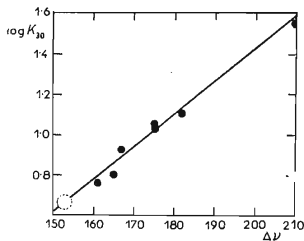
FIG. 2

Relationship between Association Constant of the System Substituted Phenol–Valeronitrile in Tetrachloromethane and the Phenol OH Frequency Shift upon Hydrogen Bond Formation

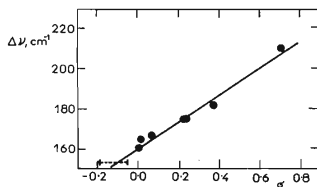Data for all the alkylphenols studied are represented by one circle.

FIG. 3

Relationship between Frequency Shift of the Phenol OH Fundamentals Vibration upon Hydrogen Bond Formation with Valeronitrile and Hammett Constant σ

Data for all the alkylphenols studied are represented by one circle.

with the frequency shifts $\Delta\nu$ (Fig. 2). As far as it would be possible to draw conclusions from so comparatively narrow interval ($\Delta\nu = 150$—$210 \, cm^{-1}$), it seems that the change in the standard free enthalpy $-\Delta G$ is not directly proportional to but linearly dependent on, the frequency shifts. The linear relationships between $\log K$ and σ and between $\log K$ and $\Delta\nu$ imply that also $\Delta\nu \, vs \, \sigma$ are linearly dependent (Fig. 3). It can be therefore concluded that the association of *meta*- and *para*-substituted phenols with valeronitrile is in harmony with common concepts on formation of complexes via hydrogen bonding and further that both association equilibria and chemical reactivity of these compounds are affected by electronic effects of substituents in a similar way.

REFERENCES

1. Pimentel G. C., McClellan A. L.: *The Hydrogen Bond*. Freeman, San Francisco 1960.
2. Kempter H., Mecke R.: Z. Physik. Chem. (Leipzig) B *46*, 229 (1940).
3. Fritzsche H.: Z. Chem. *1*, 263 (1961).
4. Adámek P., Ksandr Z.: Sborník VŠCHT Prague H *5*, 91 (1969).
5. Brändström A.: Acta Chim. Scand. *10*, 1197 (1956).
6. *International Critical Tables of Numerical Data — Physics, Chemistry and Technology*, Vol. III, p. 28. New York 1928.
7. Eckschlager K.: *Errors, Measurement and Results in Chemical Analysis*, p. 143. Van Nostrand Reinhold, London 1969.
8. Hammett L. P.: *Physical Organic Chemistry*. Mc Graw Hill, New York 1940.
9. Exner O.: Chem. listy *53*, 1302 (1959).
10. Taft R. W., jr in the book: *Steric Effects in Organic Chemistry*. (M.S. Newman, Ed.) Chap. 13. Wiley, New York 1956.
11. Heinen W.: *Thesis*. University Utrecht 1964.
12. Badger R. M., Bauer S. H.: J. Chem. Phys. *5*, 839 (1937).

AXIAL DISPERSION IN A REACTOR WITH A HELICAL FLOW

T. SÁKRA[a], F. LEŠEK[b] and H. CERMÁNKOVÁ[c]

[a] *Institute of Chemical Technology, Pardubice,*
[b] *Research Institute for Synthetic Resins and Lacquers, Pardubice*
[c] *Mrazirny, Litoměřice*

The magnitude of the axial dispersion belongs to basic problems in designing reactors for chemical reactions with reaction products of molecular masses depending considerably on time spent in the reactor. If the flow in such a reactor differs remarkably from the piston flow, a high molecular weight product of some polycondensation may for example stick on the reactor walls.