COMPARISON OF PENTACHLORO- AND PENTAFLUORO-PHENOLS AS PROTON DONORS WITH THE AID OF IR SPECTRA

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After the investigations [1] and a number of subsequent investigations which established a direct correlation between the low-frequency shift of the νAH band of a standard proton donor in the formation of a hydrogen bond and the basicity of the proton acceptor, wide acceptance has been acquired of the view of the hydrogen bond as interaction of the acid – base type whose qualitative and quantitative characteristics are determined by the acidity and basicity of the partners [2]. Investigation of the hydrogen bond with the participation of hydrogen halides [3] and hydroxy and mercapto compounds [4, 5] as proton donors has shown that in these series increase in acidity is accompanied by weakening of the hydrogen bond, so that acidity cannot be used as a universal measure of the ability of an RAH molecule to form a bond of the type RAH...B (proton-donor power), at least in series of compounds with different A atoms. Our task in the present work was the spectroscopic investigation of the interaction of two OH-containing donors, pentachlorophenol (I) and pentafluorophenol (II), with various proton acceptors with the object of determining the thermodynamic characteristics of the complexes. The phenol (I) is a stronger acid than the phenol (II) (pK_a 5.2 and 5.5 respectively [6]), and therefore special interest is evoked in the first place by the comparison of their abilities to form a hydrogen bond. Much material has been published in recent years on the energies of hydrogen bonds of chlorophenols, including (I), with proton acceptors [7, 8], but as the main purpose of our work lay in the close comparison of the proton-donor powers of the phenols (I) and (II) we considered it desirable to carry out all the measurements for both phenols, for by the use of unified procedure the accuracy of of the thermodynamic parameters is raised substantially. As acceptors we chose members of various classes or organic compounds, covering a wide range of electron-donor power: acetonitrile, butanone, tetrahydrofuran, pyridine, dimethyl sulfoxide, and trimethylphosphine oxide. An important feature of (I) [9] and also, as the present work shows, (II) is that their interaction with the stronger organic bases, e.g., with aliphatic amines, in nonpolar solvents (CCl_4) leads to the transfer of the proton from the hydroxy group of the phenol to the acceptor with formation of an undissociated ion pair. It was therefore of interest to compare the acidities of (I) and (II) with the thermodynamic parameters characterizing not only their strengths as partners in a hydrogen bond, but also their ability to donate a proton to the acceptor with formation of an ion pair. There are no data of this kind for complexes of (II) with amines. The enthalpy of formation of the complex of (I) with tributylamine has been measured calorimetrically [10]. So far as we know, no spectroscopic measurements of the thermodynamic characteristics of complexes of this type have been made. An exception is to be found in our previous investigation [9] on the vibrational spectra and structure of complexes of (I) with secondary amines, when we gave preliminary estimates of equilibrium constants and enthalpies of formation of ion pairs. In the present work we have carried out more careful measurements and obtained more precise values of the thermodynamic constants for the complexes of (I) and (II) with dibutylamine and trioctylamine.

EXPERIMENTAL

The IR spectra in the νOH region were determined for CCl_4 solutions containing phenol and acceptor with a UR-20 spectrometer. The equilibrium constants of the reactions

$$C_6Hal_5OH - B \rightleftharpoons C_6Hal_5OH \cdots B \quad \text{or} \quad C_6Hal_5OH + B \rightleftharpoons C_6Hal_5O^- \cdots HB^+ \tag{1}$$

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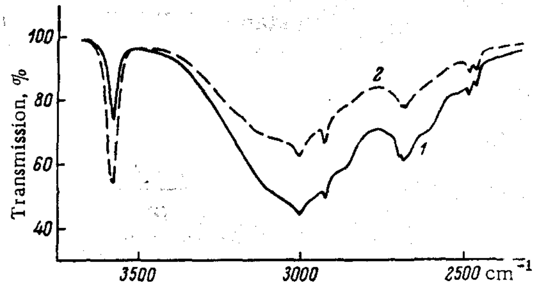

Fig. 1. Spectra of the system (II) + dimethyl sulfoxide (0.0051 and 0.0061 mole/liter) in CCl_4 at 22° (1) and 72° (2); d 5 mm.

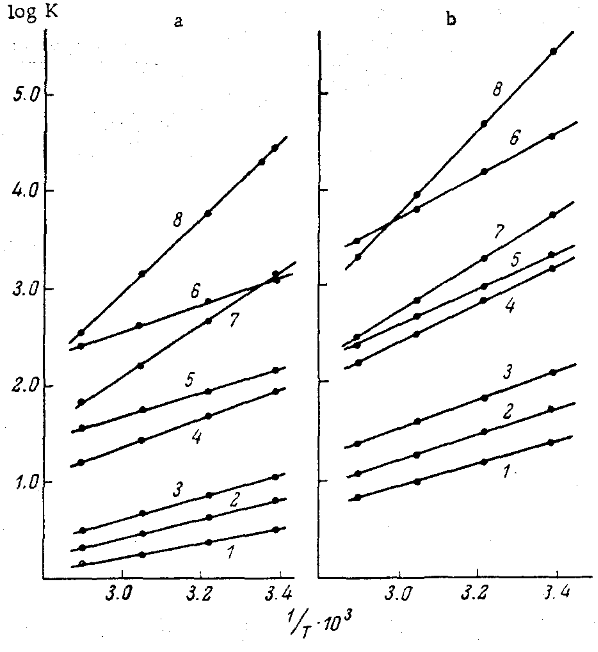

Fig. 2. Relation of log K to 1/T for (I) (a) and (II) (b) with acetonitrile (1), butanone (2), tetrahydrofuran (3), pyridine (4), dimethyl sulfoxide (5), trimethylphosphine oxide (6), trioctylamine (7), dibutylamine (8).

taking account of the balance equations can be represented in the form

$$K = \frac{c^{ab}}{c^a c^b} = \frac{c_0^a - c^a}{c^a\,[c_0^b - (c_0^a - c^a)]},$$

in which c^{ab}, c^a, c^b are the concentrations of the complex, free phenol molecules, and the proton acceptor respectively and c_0^a and c_0^b are the initial concentrations of the components. For the determination of K it is sufficient to measure the number of free phenol molecules c^a. The measurements were based on the optical densities of the bands of the monomers of (I) at 3525 cm^{-1} and of (II) at 3573 cm^{-1}. In the working range of concentrations of phenols (0.002-0.6 mole/liter) the optical density of the νOH band rises linearly with concentration, while the band of associated phenol molecules is not observed; the self-association of the phenol can therefore be neglected. The absorption coefficient at the maximum of the νOH band of the phenol monomer decreases with rise in temperature; this dependence was taken into account in the determination of c^a at each temperature. In the measurement of absorption coefficients, as also in the calculation of the equilibrium coefficient, a correction was introduced for the dependence of c_0^a and c_0^b on temperature on account of the change in the density of the solvent. The value of K was found in several experi-

TABLE 1. Equilibrium Constants at 22°, Enthalpies of the Formation of a Hydrogen Bond of (I) and (II) with Proton Acceptors, and Shifts in the νOH Band of the Phenols in the Complexes

Acceptor	$K_{22°}$, liter/mole		ΔH, kcal/mole		$\Delta\nu$OH, cm^{-1}	
	(I)	(II)	(I)	(II)	(I)	(II)
CH_3CN	3.5	24	3.3	5.3	200	290
$CH_3COC_2H_5$	6.2	55	4.4	6.1	215	325
$(CH_2)_4O$	11.0	130	5.3	6.8	380	480
$(CH_3)_2SO$	140	2100	5.7	8.4	520	590
C_5H_5N	83	1600	6.7	9.3		
$(CH_3)_3PO$	1200	40000	6.6	10.3		

TABLE 2. Thermodynamic Characteristics of Ion Pairs Formed by (I) and (II) with Amines in CCl_4

Acceptor	(I)			(II)		
	$K_{22°}$, liter/mole	ΔH, kcal/mole	ΔS, eu	$K_{22°}$, liter/mole	ΔH, kcal/mole	ΔS, eu
$(C_8H_{17})_3N$	1340	12	26	2100	12	24
$(C_4H_9)_2NH$	27700	19	43	48100	20	42

ments with different contents of the components, and the condition $c_0^a < c_0^b$ was always observed. Analysis of the error in the determination of K by Eq. (2) showed that deviations from this condition (in particular, the use of equimolecular concentrations in [9]) for high values of K, characteristic for complexes with a strong hydrogen bond and ion pairs ($K \sim 10^3-10^4$), when $c^a \ll c_0^a$ and c_0^b, leads to a marked increase in error. Observance of the condition $c_0^a < c_0^b$ also avoids the possibility of the formation of 2 : 1 phenol–acceptor complexes. The decrease in the optical density of the νOH band of the monomer due to excess of acceptor in the system was compensated for by the use of cells with a long optical path (1-5 cm). To check the reliability of the procedure, for the case of the system (II)–dimethyl sulfoxide we carried out a parallel determination of the equilibrium constant at various temperatures with the measurement of c^{ab} from the integral intensity of the νOH band of the complex at $\sim 3000\ cm^{-1}$ (Fig. 1). The results obtained by the two methods agree well with one another. The enthalpy of the process (I) was determined from the relation of log K to 1/T, which in all cases approximated to a straight line (Fig. 2).

DISCUSSION OF RESULTS

The values found for K and ΔH of the hydrogen-bonded complexes are given in Table 1. Values of K for various systems at various temperatures are accurate within 5-20%; the error in ΔH is ~10%. The results show that for all the proton acceptors in the temperature range studied K is less for (I) than for (II). The change in enthalpy in the formation of complex is also less for (I) than for (II). This means that the proton-donor power of (II) is greater than that of (I), although the latter is the stronger acid; which is contrary to the hypothesis in [11].

Some doubts about the validity of this conclusion may arise from the existence of an intramolecular hydrogen bond in the phenols studied. Actually, for the free molecules of (I) and (II) the relation of potential energy to the angle of rotation around the C–O bond (the COH angle may also change here) has the form shown diagrammatically in Fig. 3 (continuous curves). As our zero we took the energy of the equilibrium configuration of the molecule. According to [12], the height of the barrier for rotation around the C–O bond in o-fluorophenol is lower by 0.7-0.8 kcal/mole than in o-chlorophenol; it may be supposed that this difference does not change very strongly in the change to (II), so that ΔE in Fig. 3 probably does not exceed 1-1.5 kcal/mole. In the formation of the intermolecular hydrogen bond OH...B the hydrogen atom of the hydroxy group of (I) moves out of the plane of the ring [13], and as a result of intermolecular interaction a potential trough is formed (shown by the broken line in Fig. 3) at values of the angle φ which do not correspond to a stable configuration in the free molecule. The quantities ΔH_1 [for (I)] and ΔH_2 [for (II)] are experimentally measurable; the quantities $\Delta H_1'$ and $\Delta H_2'$ represent, properly speaking, the strength of the

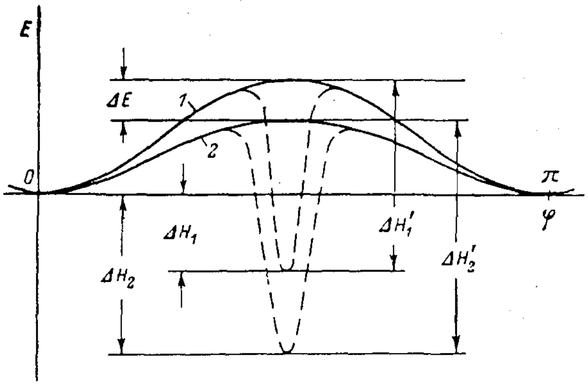

Fig. 3. Internal-rotation potential curves for (I) (1), (II) (2), and their hydrogen-bonded complexes (broken line).

hydrogen bond formed by the OH group of the phenol molecule with the same divergence from the plane of the ring as will ensure a complex of minimum energy.

Further arguments in support of the conclusion of the higher proton-donor power (in the sense of hydrogen-bond formation) of (II) than (I) can be obtained from an analysis of the shift in the νOH frequency of these phenols in the formation of the complex. As well as the enthalpy, the magnitude of the shift is often used as a measure of proton- and electron-donor powers [14]. Values of $\Delta\nu$ are given in Table 1. For the strong acceptors pyridine and trimethylphosphine oxide the band has a great width and complex structure, and the determination of the position of its center with sufficient accuracy was not found possible. From Table 1 it follows that for each acceptor $\Delta\nu$OH is less for (I) than for (II). According to [15] in the formation of complexes with $(C_6H_5)_3PO$ the νOH band of (II) is more strongly shifted toward the low frequencies than the band of (I), while the intensity of the νOH band of the monomer of (II) is less under like conditions. These facts also point to the higher proton-donor power of (II) than of (I). The order of the electron-donor powers of the molecules studied both toward (I) and toward (II) $[CH_3CN < CH_3COC_2H_5 < O(CH_2)_4 < (CH_3)_2SO < C_5H_5N \approx (CH_3)_3PO]$ is the same as that given in [16].

Table 2 gives the thermodynamic parameters of the ion pairs formed by (I) and (II) with $(C_8H_{17})_3N$ and $(C_4H_9)_2NH$. It can be seen that, although the quantities K and ΔH have close values for (I) and (II) (for the complexes with $(C_8H_{17})_3N$ the difference in ΔH lies within the limits of experimental error), in this case also, (II) is a somewhat stronger proton donor than (I), and correlation with pK_a values is not observed. On the other hand, the high proton-acceptor power of the secondary amine in comparison with the tertiary amine is noteworthy. This fact was pointed out previously [17]. Hence, in spite of the fact that acidity and proton-donor power, understood as the ability to donate a proton with formation of an ion pair, appear in their physical sense to be characteristics of the molecule that are closer to one another than acidity and the ability to form a hydrogen bond, there are nonetheless substantial differences between them. These differences are probably mainly determined by the difference in the character of the interaction of an anion with a cation and with the surrounding medium in aqueous solution and in an ion pair in a low-polarity solvent.

CONCLUSIONS

1. The thermodynamic characteristics of complexes of pentachlorophenol (I) and pentafluorophenol (II) with various proton acceptors were determined from the IR absorption spectra.

2. For all the acceptors investigated the equilibrium constants and enthalpy changes in the formation of a hydrogen-bonded complex are less in the case of (I) than in the case of (II). Hence, the proton-donor power understood as the ability to form a hydrogen bond is greater for (II) than for (I), although the latter is the stronger acid.

3. In spite of the fact that acidity and the ability to donate a proton with formation of an undissociated ion pair are close in meaning as characteristics of proton-donor molecules, again no correlation is observed between the pK_a values of the phenols investigated and the thermodynamic characteristics of the ion pairs formed with their participation.

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