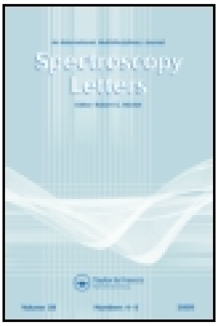

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INFRARED STUDY OF THE INTERACTION OF PENTACHLOROPHENOL WITH SECONDARY AMINES.

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In connection with the possibility of spectroscopic study of equilibria, caused by the proton transfer in hydrogen bond[I], of great interest are the amine-phenol systems. Increasing of the protonodonating power of the OH phenol group necessary for the proton transfer to occur could be obtained by introducing electronegative substituents into the ring. According to[2,3] the protonodonating power in the series of phenol chloroderivatives widely ranges, pentachlorophenol (PCP) being the most active donor of a proton in the series.

To clarify the structure of the complexes formed by the interaction of PCP with secondary aliphatic amines there have been studied the infrared spectra of PCP + R_2NH ($R=C_2H_5$, C_3H_7, C_4H_9) and PCP + $(CH_2)_5NH$ solutions in CCl_4 and $CHCl_3$. To determine spectral characteristics of the PCP-ion and dialkylammonium ion, formed by the proton transfer in the hydrogen bond OH...N, the spectra of sodium pentachlorophenolate and amine hydrochlorides have also been examined.

The spectra of the solutions in the region I550-3600 cm^{-I} are shown in fig.I. A sharp decrease in the intensity of the νOH band in the presence of equimolar amount of amine shows the number of free molecules in the system to be small. Con-

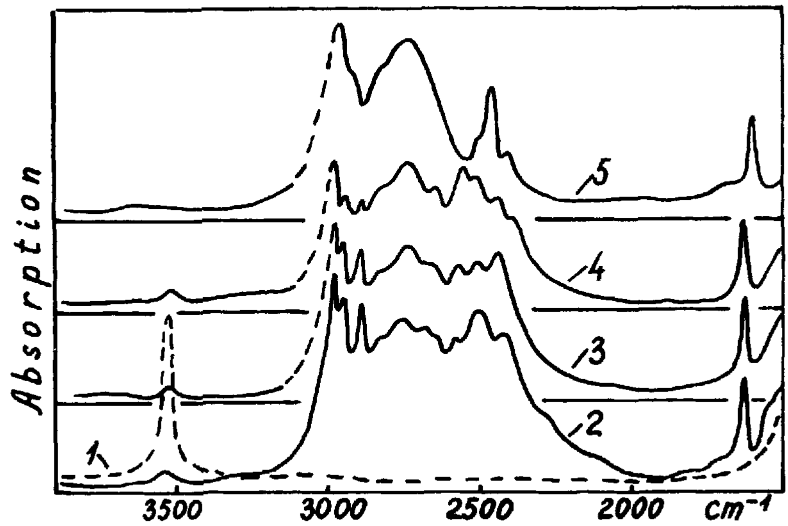


FIG. I
The spectra of solutions (0,05 M) I.C_6Cl_5OH in CCl_4, 2.C_6Cl_5OH + $(C_4H_9)_2NH$ in CCl_4, 3.C_6Cl_5OH + $(C_3H_7)_2NH$ in $CHCl_3$, 4.C_6Cl_5OH + $(C_2H_5)_2NH$ in $CHCl_3$, 5.$(C_2H_5)_2NH \cdot HCl$ in $CHCl_3$.

spicuous is the appearance of the band at 1625 cm^{-1}. The formation of hydrogen-bonded molecular complexes or charge-transfer complexes (with J_2, for instance) by secondary amines is not accompanied by the appearance of any bands near 1600 cm^{-1}. At the same time the spectra of dialkylammonium salts both in the $CHCl_3$ solution (fig.I) and in the solid state[4] shows the characteristic band near 1590 cm^{-1}, assigned to the NH_2^+ bending vibration. The frequency of the δNH_2^+ band in the spectra of proton transfer complexes of carboxylic acids with secondary amines is 1620 cm^{-1} [5,6]. The band at 1625 cm^{-1}, therefore, can be interpreted as δNH_2^+ in the dialkylammonium ion, formed due to the proton transfer from OH group of PCP to the nitrogen atom of the amine. This conclusion is justified by the experiments on C_6Cl_5OD and $(C_4H_9)_2ND$, in which case the band at 1625 cm^{-I} disappears, with the band at 1172 cm^{-I} appearing.

The spectrum in a lower-frequency region also has some features showing the formation of ionic compounds. In the presence of amine the bands II99 and I280 cm^{-I} assigned to the interacting νC-O and δO-H vibrations[7] (960 and I249 cm^{-I} in the case of C_6Cl_5OD) vanish (fig.2). Instead the band at I2I0 cm^{-I} as well as some new bands in the region I300-I600 cm^{-I} (I364, I420, I540 cm^{-I}) appear. These bands are also observed in the spectrum of solid sodium pentachlorophenolate and its ethanolic solution. The band at I2I0 cm^{-I} is attributed to the νC-O$^-$ vibrations of PCP-ion[7], while the bands near I300-I600 cm^{-I} seem to belong to in-plane skeletal modes. Characteristic changes are observed in the amine spectrum as well. In the presence of PCP the band ν_aC-N 1140 cm^{-I} [8] is replaced by the bands in the region I050-I070 cm^{-I}, similar to those

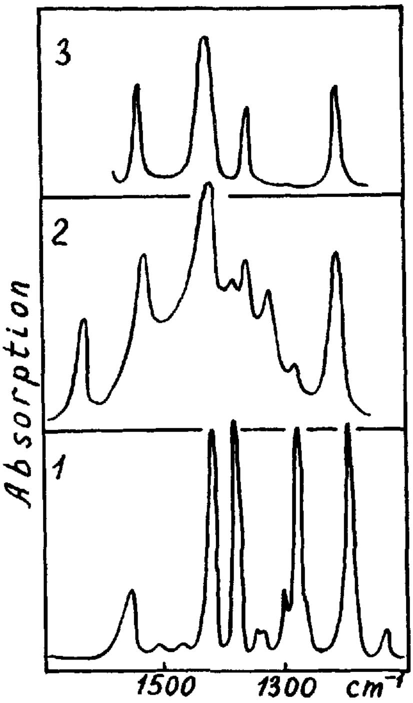


FIG. 2
The spectra of I.C_6Cl_5OH in CCl_4 0,05 M, 2.C_6Cl_5OH + $(C_3H_7)_2NH$ in CCl_4 both 0,05 M, 3.C_6Cl_5ONa solid.

in the diethylammonium hydrochloride spectrum (fig.3). As was shown in[9], the formation of secondary amine salts leads to the 70–I00 cm^{-I} shift of the ν_a C-N band toward low frequencies. A crystalline precipitate have been obseıved to form in CCl_4 solutions of C_6Cl_5OH + $(C_2H_5)_2NH$ and $C_6Cl_5OH + (CH_2)_5NH$. The spectroscopic study showed it to be ionic compound. Thus, one can draw the conclusion, that the interaction of PCP with secondary amines is accompanied by the proton transfer from OH group of PCP to the nitrogen atom of the amine with the formation of the ionic pair. No dissociation of ionic pairs in low dielectric solvents practically occurs[IO], so the concentration of free ions in the systems concerned is negligibly small. The bands of hydrogen-bonded molecular complex have not been observed.

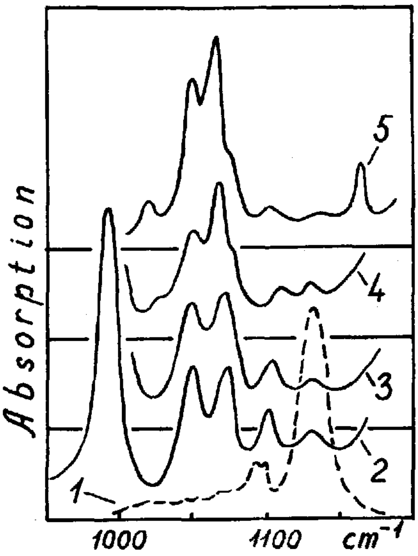


FIG. 3
The spectra of 0,I M solutions I.$(C_3H_7)_2NH$ in CCl_4, 2.$(C_4H_9)_2NH + C_6Cl_5OH$ in CCl_4, 3.$(C_3H_7)_2NH + C_6Cl_5OH$ in $CHCl_3$, 4.$(C_2H_5)_2NH$ + C_6Cl_5OH in $CHCl_3$, 5. 5.$(C_2H_5)_2NH\cdot HCl$ in $CHCl_3$.

There have been studied the temperature and concentration dependence of the spectra of $C_6Cl_5OH + (C_3H_7)_2NH$ solution in $CHCl_3$ and $C_6Cl_5OH + (C_4H_9)_2NH$ solutions in $CHCl_3$ and CCl_4. The increase in temperature, as well as the decrease in concentration results in the rise of the intensity of the free molecules bands, particularly νOH 3524 cm^{-I} and the weakening of the ion-pair bands. No new bands, which could be attributed to the molecular complex, appear. Measurements of the intensity of νOH and δNH_2^+ bands showed, that within the errors of the experiment the increase of the free molecules concentration was equal to the decrease of the concentration of ionic pairs. Hence the latter are in equilibrium only with free molecules:

$$C_6Cl_5OH + R_2NH \rightleftharpoons C_6Cl_5O^- \ldots H_2N^+R_2 \qquad (I)$$

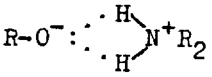
No complexes containing more than one molecule of PCP were found to form. The thermodynamic characteristics of the equilibrium (I) have been obtained by measuring the concentration of free molecules at different temperatures, there being used the νOH band of PCP. The absorption coefficient ε_{OH} of this band is independent of the concentration and equal to 4,7.I0^2 and 3,95.I0^2 l/mole.cm at 20°C in CCl_4 and $CHCl_3$ solutions respectively. In treating the data obtained the temperature dependence of ε_{OH} (decreasing by ~7% in $CHCl_3$ and by ~I2% in CCl_4 in the interval I0-60°C) was taken into account. For quantitative treating the experiments were used where the initial concentrations C_0 cf PCP and amine were equal. Then the equilibrium constant K is as follows:

$$K = \frac{C_{ip}}{C_{PCP} \cdot C_A} = \frac{C_0 - C_{PCP}}{C_{PCP}^2}$$

where C_{ip} , C_{PCP} and C_A are the concentrations of the ionic pairs and free molecules of PCP and amine respectively. The values K measured for all the systems concerned do not depend on the concentration from 0,I to 0,0I M. The plot lnK vs I/T in the interval I0-60°C is a straight line. The enthalpy ΔH and the entropy ΔS of the ionic pair formation, as well as their rms deviations, determined by the least square method are given in the table. Also given in the table are the values of K at 20°C. The ΔH and K values at any temperature are less for PCP-dibutylamine system in $CHCl_3$ than in CCl_4 solution, though the dielectric constant of chloroform is higher. Since the ΔH value, obtained in the experiment is defined by the energy difference between the initial and final states, this decrease is stipulated by free molecules and ionic pair interaction with the solvent. In $CHCl_3$ compared with CCl_4 solution the energy level of free molecules is reduced chiefly by the formation of hydrogen bond $Cl_3CH...N$, whose energy is ~4 kcal/mole[II]. The level of the ionic pair is also reduced in $CHCl_3$, but the energy gain seems less than in the case of free molecules. This shows, that the dielectric constant of the medium is not decisive in the energetics of the proton transfer reaction studied. Most important here is the intermolecular interaction with the solvent (see also[I]).

PCP + R_2NH	Solvent	$K_{20°C} \cdot 10^{-3}$ l/mole	$-\Delta S$ e.u.	$-\Delta H$ kcal/mole
$R=C_3H_7$	$CHCl_3$	7±I	II,0±0,6	8,4±0,4
C_4H_9	$CHCl_3$	II±I	11,4±I,0	8,8±0,6
C_4H_9	CCl_4	28±6	I9,0±I,0	II,5±0,6

The most probable structure of the ionic pair, formed in the proton transfer from PCP to amine is as follows:



$$R\text{-}O^{-}:\!:\!\begin{smallmatrix}H\\H\end{smallmatrix}\!>N^{+}R_2 \qquad (II)$$

Then the two wide bands with maxima at about 2520 and 2730 cm^{-I}, having a complicated structure (fig.I) may be interpreted as ν_s and ν_a of the NH_2^+ group. The complex with asymmetrical group NH_2^+ where one hydrogen atom interacts with an oxigen atom, while the other either interacts with chlorine atom or even is in no direct contact with the anion at all, should have had the ν NH band in a higher-frequency region. Besides in the latter case the free group NH is to be rather a strong proton donor and to interact easily with any acceptor. Yet, when the ethylacetate was added to the solution under investigation, no changes of its ν C=O band sensitive to the hydrogen bond formation were observed. Thus the structure (II) seems to be preferable.

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