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COMPARATIVE CHARACTERISTICS OF THE PROTON-DONOR CAPABILITY OF BENZOIC ACID AND ITS PENTACHLORO- AND PENTAFLUORO-SUBSTITUTED DERIVATIVES

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In recent years the methods developed for determining the energy of the complexes formed between carboxylic acids and proton acceptors in inert solvents have been used to study the effect of a substituent on the proton-donor capability of halogen-substituted fatty acids [1-4]. A comparison of the proton-donor capability of benzoic acid (BA) and its pentachloro- (PCBA) and pentafluoro- (PFBA) substituted derivatives, in which the mechanism of the effect of the substituent is more complex than in aliphatic compounds, was the goal of this paper: The variations in the proton-donor capability are governed by competing factors which have effects in opposite directions. Of special interest is a comparison of the proton-donor capability and acidity of halogen-substituted benzoic acid, because no correspondence between these values was found for pentachloro- and pentafluoro-substituted phenol: The former is a stronger acid, but forms a less stable hydrogen bond with a given acceptor than the latter [5].

The thermodynamic characteristics of the complexes formed between BA, PCBA, and PFBA and acetonitrile, methyl ethyl ketone, tetrahydrofuran, and dimethyl sulfoxide in a CCl_4 solution were measured from their IR absorption spectra. Since the dimers of the acid also exist in the solution along with the complexes over the operating temperature and concentration ranges, then in order to determine the equilibrium constant K of the reaction

$$RCOOH + B \rightleftarrows RCOOH \ldots B \qquad (1)$$

from the ν_{OH} band of the acid monomer

$$K = \frac{C^{ab}}{C^a C^b} = \frac{C_0^a - C^a - C_d^a}{C^a [C_0^b - (C_0^a - C^a - C_d^a)]}$$

(C_0^a, C_0^b are the starting concentrations of the acid and acceptor, C^a is the concentration of the free acid molecules, C_d^a is the concentration of the acid dimers), one must also know the value of C_d^a. The values of C_d^a were determined as in [6] using the dimerization constants of the acid obtained in [7] under analogous experimental conditions. The spectra of the solutions containing 0.001-0.0025 mole/liter of acid and 0.003-0.4 mole/liter of the proton acceptor were obtained in the ν_{OH} region. The measurement of C^a was carried out from the peak intensity of the ν_{OH} band of the monomeric acid molecules because the halfwidth of this band is independent of temperature over the 22-85°C temperature range [7]. The values of K for each system was measured at 22, 38, 55, 72, and 85°C (the cells used, which were of constant size, allowed us to work at

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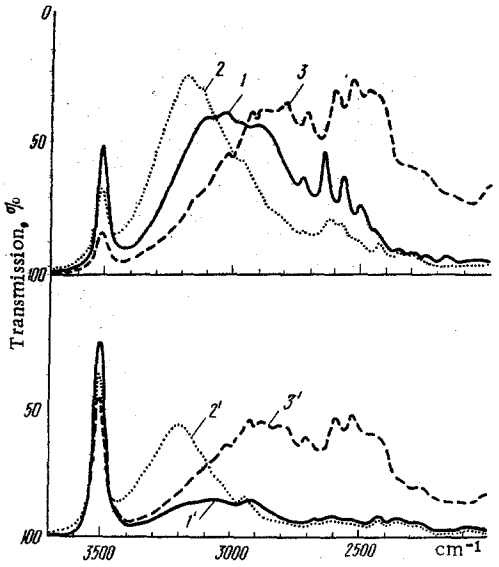

Fig. 1. IR spectra of CCl_4 solutions: 1) PFBA (0.0024 mole/liter); 2) PFBA (0.0024 mole/liter) + acetonitrile (0.104 mole/liter); 3) PFBA (0.0024 mole/liter) + dimethyl sulfoxide (0.003 mole/liter) (d = 2 cm, 22°C); 1', 2', 3') the same at 85°C.

TABLE 1. Equilibrium Constants (at 22°C) and Changes in Enthalpy and Entropy During the Formation of a Hydrogen Bond between Benzoic Acid, Its Pentachloro and Pentafluoro Derivatives, and Proton Acceptors

Acceptor	C_6H_5COOH			C_6Cl_5COOH			C_6F_5COOH		
	K, liters/mole	$-\Delta H$, kcal/mole	$-\Delta S$, cal/mole·deg	K, liters/mole	$-\Delta H$, kcal/mole	$-\Delta S$, cal/mole·deg	K, liters/mole	$-\Delta H$, kcal/mole	$-\Delta S$, cal/mole·deg
CH_3CN	4,2	3,4	8,6	12	4,3	9,6	34	5,4	11,1
$CH_3COC_2H_5$	12	4,3	9,5	35	5,2	10,5	110	6,2	11,7
$(CH_2)_4O$	38	5,2	10,4	98	6,0	11,3	360	7,2	12,6
$(CH_3)_2SO$	1000	7,8	12,6	2900	8,8	14,0	12600	9,7	14,1

temperatures exceeding the boiling point of the solvent by 20-30°C). The changes in the spectra of the acid in the presence of acetonitrile and dimethyl sulfoxide at the extreme temperatures are shown in Fig. 1. The values of K at each temperature were determined from several experiments for various ratios between C_0^a and C_0^b. No systematic changes in K as a function of C_0^a and C_0^b were detected. The deviations of the value of K from the average value K_{av} lie in the 10-20% range. The enthalpy of process (1) was determined from the dependence of log K on 1/T, which was a straight line in each case. The error in determining ΔH and ΔS comes to 10-15%. The results obtained are given in Table 1, from which it is evident that the values of K and ΔH for each proton acceptor increase in the series BA, PCBA, and PFBA; i.e., the proton-donor capability increases in this series. This same conclusion follows from the change in the magnitude of the low-frequency shift of the ν_{OH} band of these acids during the formation of a complex with a given proton acceptor. For example ν_{OH} decreases by 240, 280, and 310 cm^{-1}, respectively, for the BA, PCBA, and PFBA complexes with acetonitrile compared to the frequency of the acid monomer in CCl_4. This order of magnitude is retained for the other acceptors.

The results obtained show that PCBA forms a less stable hydrogen bond RCOOH...B than PFBA, as in the case of the pentahalogenated phenols [5], although its acidity is higher [8]. According to the data in [9, 10], the proton-donor capability of monohalogen-substituted (para and meta) phenols agrees with their acidity; in each case the fluorophenol is not a stronger proton donor than the chlorophenol. Therefore, it can be presumed

that the anomaly detected in [5] is due to the nonplanar structure of the complex with the intermolecular hydrogen bond $C_6Hal_5OH...B$ in which the hydrogen atom of the hydroxyl group emerges from the plane of the ring. This leads to a change in the structure of the π-electron system and this can affect the proton-donor capability of the hydroxyl group in pentachloro- and pentafluorophenol in different ways.

The results obtained with pentahalogen-substituted benzoic acids permit one to conclude that this effect cannot be the only reason for the absence of correspondence between the acidity and proton-donor capability of the OH group. Actually in the case of the acids there is no basis to assume that the formation of the hydrogen bond $C_6Hal_5COOH...B$ should be accompanied by such a change in the geometry of the molecule as would entail a substantial redistribution of the electron density in the system and, as a result, a change in the proton-donor capability differing for PCBA and PFBA.

Evidently a comparative investigation of the proton-donor capability of chloro- and fluoro-substituted phenol and benzoic acid containing no substituents in the ortho position could yield additional data to clarify the molecular nature of the anomalies detected.

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