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STRUCTURE AND ENERGETICS OF COMPLEXES OF 2-HEPTAFLUORONAPHTHOL WITH ALIPHATIC AMINES IN A HYDROCARBON SOLVENT

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In a study of the role of the hydrogen bond in intermolecular proton transfer processes, it is important to examine the structure of the complexes formed by strong proton donors with strong acceptors in inert solvents and in a gas phase, and to clarify the types of equilibria existing in these systems [1]. Suitable materials for these investigations may be polyfluorinated naphthols with a high proton-donor ability [2, 3], a favorable disposition and form of the electronic absorption spectrum in the near UV region [4, 5], and high thermal stability up to 200-350°C [4].

In the present work, we report the results of the investigation on the structure of complexes formed by 2-heptafluoronaphthol $C_{10}F_7OH$ (HFN) with secondary and tertiary aliphatic amines in a solution in alkanes according to IR and UV absorption spectra in the range of 20-170°C, and submit the values of the equilibrium constants of the formation of molecular and ionic complexes and the corresponding changes in the enthalpy and entropy, obtained from the spectral data. Alkanes belong to the group of the most inert solvents, in which the formation of ionic adducts with a passed-over proton can be very much impeded. However, because of the poor transparency in the IR region, the use of IR spectroscopy for the determination of the structure of the complex is greatly restricted. Spectra in the UV region can, in general, be used to accurately record an ionic complex. Its formation is usually accompanied by considerable changes in the electronic spectrum, but only in rare cases is it possible to detect in the UV spectrum a molecular complex with a hydrogen bond and to measure its concentration in systems with a proton transfer. Therefore, in the present work, we used an approach [6] based on the simultaneous use of IR and UV spectra: the number of the free molecules of the proton donor is determined from ν_{OH} band in the IR spectrum and the concentration of the ionic pairs, from the band of the ionic form in the UV spectrum, while the number of the molecular complexes with a hydrogen bond is found from the balance. Since to understand the proton transfer mechanism, data on the structure of a bimolecular donor—proton acceptor complex are most important [7, 8], the investigations were carried out under conditions at which the formation of more complicated complexes containing two or more donor molelcules, i.e., at a considerable excess of the amine is maximally impeded.

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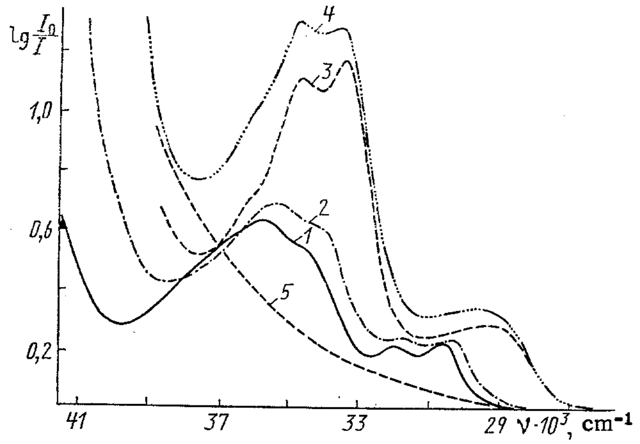

Fig. 1. UV absorption spectra of 2-heptafluoronaphthol solutions ($1.5 \cdot 10^{-4}$ mole/liter) at 20°C: in undecane (1), dimethyl sulfoxide (2), undecane in the presence of $1.5 \cdot 10^{-2}$ mole/liter of trioctylamine (3), in water in the presence of $3.0 \cdot 10^{-3}$ mole/liter of KOH (4). Absorption of a trioctylamine solution ($1.5 \cdot 10^{-2}$ mole/liter) in undecane (5). Layer thickness 1.0 cm.

The UV spectrum of HFN in hydrocarbon solvents (hexane, octane, undecane) agrees with the data given in [5]. The form of the spectrum and its position are similar to those of 2-napthol $C_{10}H_7OH$, which generally characterizes the perfluoro aromatic compounds [4]. The vibrational structure of the HFN bands is less distinctly expressed than it is in the case of 2-naphthol, and therefore the formation of even a strong hydrogen bond OH...B does not lead to appreciable changes in the spectrum (Fig. 1). These could serve as a reliable qualitative identification and quantitative determination of the spectral and thermodynamic characterististis of the complex, as occurred, for example, in [9] for the complexes of 2-naphthol with proton acceptors. Figure 1 shows that in the formation of a hydrogen bond with dimethyl sulfoxide (DMSO), the HFN band is shifted by about 200-250 cm^{-1} to the low frequency region, its intensity increases slightly, and its structure is somewhat blurred. Similar changes are observed also in the spectra of HFN solutions in dioxane, diethyl ether and other oxygen-containing solvents.

In the presence of aliphatic amines, the form of the spectrum changes considerably: new bands appear which are shifted by 2000-2500 cm^{-1} to lower frequencies (Fig. 1). Their intensities increase with increase in the concentration of the amine. In the presence of excess amine, the spectrum is very similar to that of an aqueous solution of HFN containing KOH, and hence, it belongs to the HFN anion. This means that in a hydrocarbon solvent, the proton is transferred from the OH group of naphthol to the amine nitrogen atom with the formation of an ionic complex. Since at all frequencies in the working region, the absorption coefficient of the HFN anion is higher than that of its molecular form, the spectra in the UV region can be used for direct measurement of only the concentration of the ionic complexes, and the problem of the existence of molecular complexes with an OH...N hydrogen bond must be solved indirectly, starting from the known overall concentration of HFN and measuring the number of ionic complexes and free molecules of naphthol.

The measurment of UV spectra of HFN solutions in undecane containing different amounts of amine (Fig. 2) shows that in the presence of excess amine (for secondary amines ~1:3, for tertiary ~1:50), the spectrum of the ionic form no longer intensifies and does not differ from that of a solution in amine. Under these conditions, the concentration of free HFN molecules is negligibly small, and all the naphthol is bound into a complex with amine. This is seen from the IR spectra in the 3650-3500 cm^{-1} region, which includes the ν_{OH} band of the monomeric HFN molecules (Fig. 3a). In the presence of excess amine, this band is absent, and it only appears again when the temperature is appreciably increased. In the UV spectrum of HFN in an presence of excess trioctylamine (TOA) at 90-170°C, the 28700 cm^{-1} band of the anion weakens appreciably, and the band of the molecular form at 30400 cm^{-1} becomes noticeable (Fig. 3b). This band is shifted slightly into the low frequency region and is

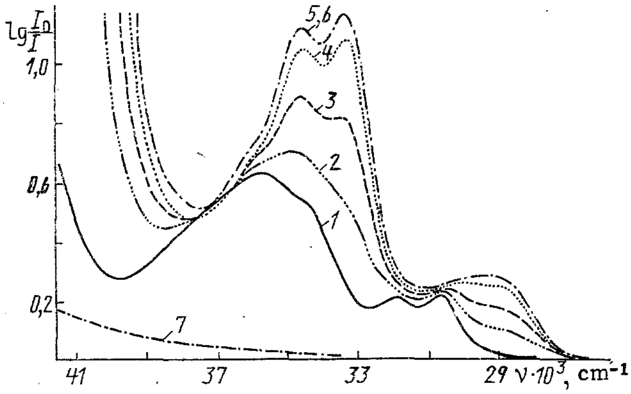

Fig. 2. UV absorption spectra of 2-heptafluoronaphthol solutions ($1.5\cdot10^{-4}$ mole/liter) in undecane at 20°C in the presence of dibutylamine: 0 (1), $3.8\cdot10^{-5}$ (2), $7.5\cdot10^{-5}$ (3), $1.5\cdot10^{-4}$ (4) $7.5\cdot10^{-4}$ (5), and $1.5\cdot10^{-3}$ mole/liter (6). Absorption of dibutylamine solution ($1.5\cdot10^{-3}$ mole/liter) in undecane (7) Layer thickness 1.0 cm.

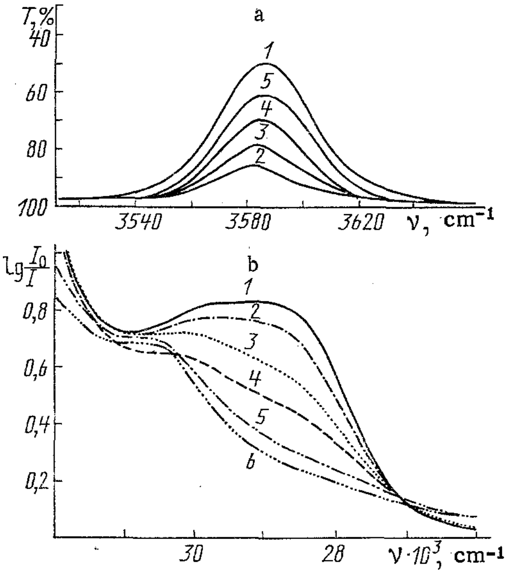

Fig. 3. Temperature changes in the absorption spectra of 2-heptafluoronaphthol solutions in undecane in the presence of trioctylamine: a) IR ν_{OH} region of monomeric molecules. HFN concentration $1.9\cdot10^{-2}$ mole/liter, TOA: 0 (1) and $2.9\cdot10^{-2}$ mole/liter (2-5): T = 150 (1), 90 (2) 110 (3), 130 (4) and 150°C (5); layer thickness 0.1 cm; b) UV absorption region of the anion, HFN concentration $9.7\cdot10^{-4}$ mole/liter, TOA $6.0\cdot10^{-2}$ mole/liter; T = 20 (1), 50 (2), 90 (3), 110 (4), 150 (5), and 170°C (6); layer thickness 0.4 cm.

blurred, compared with the band of an HFN solution in undecane at these temperatures, so it can be attributed to an HFN—amine molecular complex with an OH...N hydrogen bond (the IR ν_{OH} band of the free naphthol molecules is not noticeable under these conditions). Similar results were obtained with tributyl- (TBA) and dibutylamine (DBA), methylstearylamine and certain other amines.

The above facts show that in a hydrocarbon solvent, two types of complexes of HFN with aliphatic amines exist: a molecular and a ionic one, which are in equilibrium with one another.

$$ROH \ldots NR \rightleftarrows RO^- \ldots HN^+R. \quad (1)$$

At room temperature, this equilibrium is strongly shifted to the right. Increase in temperature leads to an increase in the number of molecular complexes, and hence the ionic form is energetically preferable at room temperature, as in other systems studied already [10]. Quantitative measurements were carried out in the range of 90-170°C, in which the concentrations of the two types of complexes are comparable.

The composition of the system at each temperature is described by two equilibrium constants, which can be formulated as follows:

$$AH + B \rightleftarrows AH \ldots B, \quad (2)$$

$$AH + B \rightleftarrows A^- \ldots HB^+, \quad (3)$$

$$K_1 = \frac{[AH \ldots B]}{[AH]\cdot[B]}, \quad K_2 = \frac{[A^- \ldots HB^+]}{[AH]\cdot[B]}. \quad (4)$$

The concentration of ionic pairs $[A^- \ldots HB^+]$ is determined from the band at 28700 cm^{-1} in the UV spectrum, that of the free naphthol molecules [AH], from the νOH band at 3575 cm^{-1} in the IR spectrum; the concentration of the molecular complexes [AH...B] and free amine molecules [B] are found from the balance equations for naphthol and the amine:

$$[AH_0] = [AH] + [AH \ldots B] + [A^- \ldots HB^+],$$
$$[B_0] = [B] + [AH \ldots B] + [A^- \ldots HB^+]. \quad (5)$$

Because of the considerable difference between the values of the absorption coefficients of the analytical bands in the IR and UV region, simultaneous measurements of intensities, required for calculating K_1 and K_2 are technically complex to carry out, and in the second case cuvettes must be used with a thickness of less than 0.1 mm. Therefore, the measurements in the IR and UV region were carried out with HFN solutions at different concentrations $\sim 10^{-2}$ and $\sim 10^{-4}$ mole/liter, respectively, and as an intermediate stage in the determination of K_1 and K_2 from the IR spectrum, their sum $K_a = K_1 + K_2$, which can be called the association constant, was found:

$$K_a = \frac{[AH_0] - [AH]}{[AH]\cdot\{[B_0] - ([AH_0] - [AH])\}}. \quad (6)$$

To calculate K_a from (6), it is sufficient to measure the value of [AH]. These measurements were carried out from the νOH 3575 cm^{-1} band in the IR spectra of the solution in undecane containing $(1.5\text{-}2\cdot5)\cdot10^{-2}$ mole/liter of HFN and $(2.0\text{-}7.5)\cdot10^{-2}$ mole/liter of TOA at eight temperatures in the range of 90-170°C. When processing the results, we took into account the change in the density of the solvent with temperature (according to the data in [11]), and the temperature dependence of the absorption coefficient at the maximum, measured in an HFN solution without an amine.

The absorption coefficient of the UV band of the ionic pair at 28,700 cm^{-1} was determined from the spectra of HFN and TOA solutions, and its temperature dependence was assumed to be identifical with that in the case of the change in the absorption coefficient of the band of the HFN anion in a solution of ethylene glycol containing KOH, in the temperature range of 20-170°C, taking into account the temperature dependence of the density of ethylene glycol [11]. From the spectra of the HFN—TOA system in undecane in the presence of different excess amounts of amine taken at the same temperatures as in the case of the IR spectra used for the determination of K_a, after graphical separation of the bands, we determined the concentrations of $[A^- \ldots HB^+]$ and calculated the values of K_1 and K_2. For example, at 110°C, their values are equal to 62 and 140 liters/mole, respectively. From the temperature dependence of K_1 and K_2, using the Van't Hoff law, we calculated the values of ΔH and ΔS of reactions (2) and (3). Figure 4 shows the data obtained in $\ln K\text{—}T^{-1}$ coordinates, and it is seen that the points lie satisfactorily, on straight lines. We used the parameters of linear dependence and found the values of ΔH and ΔS, which are given in Table

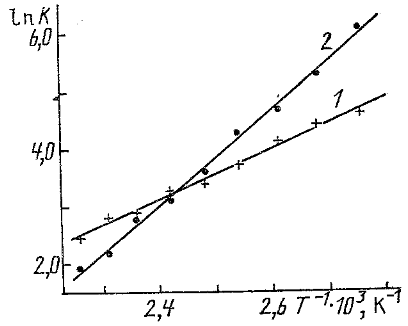

Fig. 4. **Dependences** of ln K_1 and ln K_2 of reactions of formation of molecular (1) and ionic (2) complexes in the 2-HFN—trioctylamine system in undecane on 1/T.

1. The random error of the determination of ΔH, ΔS, evaluated as 7-8% from the divergence of the points from a straight line, apparently overestimates the accuracy of the determination of the thermodynamic values by the method used. If the possible systematic errors (see for example [12] are taken into account, the accuracy of the values obtained can be evaluated as within 10-15%. Table 1 shows values similarly obtained for ΔH and ΔS of molecular and ionic complexes formed by HFN with DBA and TBA in undecane. At 110°C, the constants of these complexes are equal to: K_1 = 360 and 72 liters/mole and K_2 = 630 and 60 liters/mole, respectively. The data in Table 1 show that proton transfer in the molecular complex is accompanied by liberation of energy $\Delta H_{pr.tr.}$ 30-40 kJ/mole (8-10kcal/mole) and decrease in the entropy of the complex $\Delta S_{pr.tr.}$ 80-100 J/mole·K (20-25 cal/mole·K). These values agree well with the few data available in the literature on proton transfer along the OH...N hydrogen bond [13]. The lower values of ΔH_2 found in [2] from the IR spectra for complexes of HFN with TBA and DBA in a CCl_4 solution in the range of 20-65°C (58 and 65 kJ/mole) can be explained by an interaction between HFN and the solvent [14]. The contribution of external degrees of freedom, i.e., increase in the orderliness of the solvate shell during the formation of an ionic complex with a large dipole moment was accepted to explain the considerable decrease in the entropy of process (1) [15, 16]. In the interpretation of the results, the problem arises of the possible influence of an intramolecular interaction of a weak hydrogen bond type that exists between the hydroxyl groups and the fluorine atom in the neighboring position on the structure of the molecular and ionic complexes [4, 17]. The results of this investigation are not sufficient to indicate the orientation of the OH...N and O^-... HN^+ bonds, but it can be assumed that the rupture of the intramolecular OH...F hydrogen bond with a strength of about 4 kJ/mole [18], does not appreciably affect the experimental values of ΔH_1 and ΔH_2 for the complexes of HFN with different amines.

The differences between the thermodynamic values obtained for the three amines are small, but possibly lie within the limits determined by the accuracy of the measurements of the absolute values of ΔH, ΔS. Since, however, the influence of systemtic errors related to the measurement procedure and processing of the results affects the values of ΔH, ΔS in the same way, the relative change in some values can be fairly well described by the data in Table 1. The values of ΔH_1 for the three amines are very similar and therefore there is no sense in interpreting any tendency for them to change, but the course of the values of ΔH_2 (and $\Delta H_{pr.tr.}$) agrees with the primary spectral data (change in the band intensity of the ionic and molecular forms in the series of amines under comparable conditions at the lower section of the working temperature range), and correctly reflects the regularities in the properties of the complexes studied. A certain increase in ΔH_2 on transition from TBA to TOA is due to the higher basicity of TOA and is natural [16]. However, the increase in ΔH_2 and $\Delta H_{pr.tr.}$ for DBA, compared with the case with TBA, although it agrees with the data on the basicity of these amines in an aqueous solution, it contradicts the gas-phase basicity and the affinities to proton in the gaseous phase [19, 20]. This means that the complex of HFN with secondary amines interacts more strongly with the solvent than does the complex with tertiary amine, and this interaction initiates proton transfer in a molecular complex, ensuring a higher exothermicity of the ionic pair formation process. It is remarkable that the order of basicity of the amines in water and in a hydrocarbon solvent are qualitatively similar, despite the great differece in the mechanism and the magnitude of the interaction of the complex with the environment molecules. To clarify the reasons for this behavior of systems with a strong hydrogen bond, experimental data on the structure of complexes in the gaseous phase could be of great help.

TABLE 1. Changes in Enthalpy (kJ/mole) and Entropy (J/mole·K) during the Formation of Molecular and Ionic Complexes of 2-Heptafluoronaphthol with Aliphatic Amines in Undecane Solution

Amine	$-\Delta H_1$	$-\Delta H_2$	$-\Delta H_{\text{pr.tr.}}$	$-\Delta S_1$	$-\Delta S_2$	$-\Delta S_{\text{pr.tr.}}$
TBA	37	69	32	60	145	85
TOA	39	74	35	65	150	85
DBA	40	80	40	55	155	100

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