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THE REORGANIZATION OF THE MEDIUM IN THE REVERSIBLE PROTON TRANSFER

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SUMMARY

Results are reported of a spectroscopic study of the equilibrium $AH...B \rightleftharpoons \bar{A}..H\overset{+}{B}$, caused by reversible proton transfer in chlorophenol - tertiary amine complexes and in a molecule of 2-(diethylamino) methyl-3,4,5,6-tetrachlorophenol in glass forming solvents, and also in a monochloroacetic acid - tributylamine complex isolated in a tributylamine matrix in the temperature range 300-70 K. It has been shown that (i) the equilibrium "freezes" on the transition of a solvent into a glassy state, (ii) in a matrix, at 80 K, the state of the complex before annealing is nonequilibrium: the position of the equilibrium corresponds to a higher temperature. Both facts prove that proton transfer is accompanied by reorganization of the molecular surroundings of the complex, a more random configuration of its surroundings corresponding to the molecular form AH...B, and a more ordered configuration corresponding to the ionic pair $\bar{A}..H\overset{+}{B}$. The transition from one state to the other is possible only due to some mobility of solvent molecules.

INTRODUCTION

Spectroscopic investigations of the proton transfer in the systems with hydrogen bonding, carried out during the last two decades, have shown among other things that the structure of the complex in solutions, the type and the position of the equilibria depend considerably on the properties of the solvent (see review {1}).

For example, in non-polar or low-polar solvents (many of which are traditionally considered to be inert, such as saturated hydrocarbons, benzene, halogenated methanes, etc), the interaction of amines with carboxylic acids, chloro- or nitrosubstituted phenols, results, in many cases, in proton transfer,

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with the equilibria of two types observed {2-9}:

$$AH + B \rightleftharpoons AH...B \rightleftharpoons A^{-}..HB^{+} \qquad (1)$$

$$AH + B \rightleftharpoons A^{-}..HB^{+} \qquad (2)$$

Here, AH...B is a molecular complex with a hydrogen bond, $A^{-}..HB^{+}$ is a contact ionic pair.

At the same time, the interaction of these molecules in a gaseous phase would not proceed further than the formation of hydrogen bonded complexes. Thus, according to IR and NMR data {9,10}, in a gas phase, even trifluoroacetic acid forms the molecular complexes of the OH...N type with trimethylamine. It is only for hydrogen bromide with amine that the existance of ionic pairs in a gaseous phase was detected {11}.

Consequently, the interaction with some "inert" solvent can change the structure of a complex and the parameters of its potential surface qualitatively.

On the other hand, the study of temperature dependence of the tautomeric equilibrium.

$$AH...B \rightleftharpoons A^{-}..HB^{+} \qquad (3)$$

has shown that, generally, the transformation of a molecular complex into an ionic pair is followed by a considerable decrease of entropy (down to 20-30 e.u.) {4,8,12}. It is difficult to explain such value ΔS by means of the change in the inner sum over states of a complex, since its vibrational frequencies and rotational constants undergo comparatively small changes after the proton transfer. It is natural to suppose that the entropy change in such systems may be due to the ordering of the solvent molecules in the vicinity of the ionic pair, possessing, in comparison with the molecular complex, a considerably higher dipole moment. Some consequences, which can be tested experimentally, can be drawn from this supposition.

1. Such rearrangement of the solvate shell, accompanying the proton transfer, is possible only in case of a certain mobility of molecular surroundings of the complex. Therefore, the rate of setting the equilibrium (3) is, more or less, determined by the relaxation time of the solvent structure (τ_s). This supposition was first confirmed experimentally in {13} by the study of the temperature behaviour of the equilibrium (3) in glass forming solvents, where, by decreasing the temperature, one can reach the values τ_s essentially greater than the characteristic time of the experiment (τ_e). In this paper,

some principal results of such investigations performed with low-molecular glass forming liquids are reported. The experiments where an amorphous polymer has been used as a solvent are described in {14}.

2. If a sample is prepared by the matrix isolation method by means of codeposition of a gaseous complex and a solvent on a cooled substrate, then the equilibrium (3) has to be shifted to the molecular form of the complex in comparison with the solution which was cooled slowly to the same temperature, because of a more random arrangement of molecules of the surrounding in the matrix.

EXPERIMENT

The objects of the experiment were the complexes of chlorophenols, m-nitrophenol and monochloroacetic acid with tertiary aliphatic amines and the compound with a possible intramolecular proton transfer 2-(diethylamino)methyl-3,4,5,6-tetrachlorophenol (DMT)*. As glass forming solvents, there were used n-butanol, butyl chloride, squalane ($C_{30}H_{62}$) with glass transition temperatures T_g ~ 110, 115, 168 K respectively, as well as isopentane-methylcyclohexane and triethylamine-diethyl ether mixtures, vitrifying at ~ 83 and ~ 100 K. The solvents were purified and dried by conventional methods. The purification of solid substances was carried out by recrystallization and drying in vacuum.

The UV spectra were recorded by UV VIS Specord, and IR spectra - by UR-20 spectrophotometers. A metal cryostat with liquid nitrogen as a cooling agent was used in low temperature experiments. By means of intensive pumping out of nitrogen vapour the temperature of the sample could be decreased to 70 K. The copper holder of the cell had an electric heater fixed to it. The temperature was measured with a copper-constantan thermcouple with the accuracy 1-2°.

The matrixes were prepared by simultaneous condensation on the CaF_2 substrate of monochloroacetic acid and tributylamine in the proportion 1:20. The time of condensation was 5-10 hrs. The thickness of the layer was 0,05-0,2 mm. For liquid samples, the thickness of the layer was 0,5-5 mm.

RESULTS

Convenient objects for studying of equilibrium (3) by means of UV spectra are complexes of chlorophenols with amines. On the formation of a hydrogen

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* The UV spectra of this compound were studied in collaboration with Dr. M. Rospenk, University of Wroclaw {17}.

bond, the ^1L_b band of chlorophenol undergoes a small red shift (100-500 cm^{-1}) and its vibronic structure becomes slightly obscured {6}. On proton transfer and formation of a phenolate-ion, the shift is essentially greater (2000-3000 cm^{-1}), and the vibronic structure vanishes (fig.1-a). Fig.1-b shows the absorption spectra of solutions of 2,4,5-trichlorophenol and triethylamine in squalane. In a pronounced excess of amine, when the content of free phenol molecules is low, the appearance of the spectrum in this region is determined by two overlapping bands, near ~ 33600 and ~ 31800 cm^{-1}, belonging to trichlorophenol in a complex with OH...N hydrogen bond and to trichlorophenolate-ion in an $O^-...HN^+$ ionic pair, respectively. At room temperature, complexes of molecular type abound in the solution, since 33600 cm^{-1} band is considerably stronger. As the temperature decreases, the vibronic structure of the band becomes more pronounced, and its intensity decreases, while 31800 cm^{-1} band appears and increases in intensity, testifying to the shift of the equilibrium to the ionic pair. Like in other similar systems, proton transfer from a donor to an acceptor under such conditions is exothermic {2-9}. However,

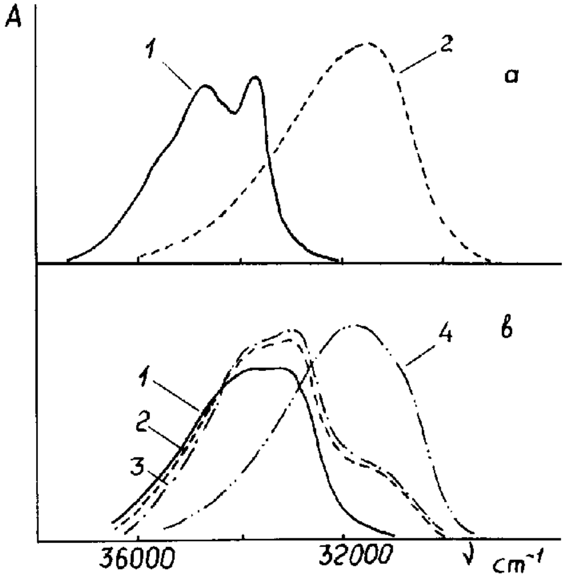


Fig. 1. Absorption spectra of solutions: a) 2,4,5-Cl_3-C_6H_2OH in cyclohexane (1) and in water with KOH (2), 300 K; b) 2,4,5-Cl_3-C_6H_2OH (2.5 10^{-3} mol/l) + $(C_2H_5)_3N$ (0.1 mol/l) in squalane, 292 K (1), 173 K (2), 70 K (3) and in isopentane-methylcyclohexane mixture, 108 K (4).

at temperatures close to the vitrifying range of squalane, redistribution of the band intensities stops, and the further decrease of temperature from T_g to 70 K does not affect the appearance of the spectrum. In the mixture of isopentane-methylcyclohexane, with a lower value of T_g, the shift of the equilibrium and redistribution of band intensities continues at lower temperatures than in a squalane. The fall of temperature to ~ 100 K leads practically to complete disappearance of the molecular complex band (fig.1-b).

Similar changes have been recorded in the spectra of other complexes with the participation of chlorophenols and tertiary amines in hydrocarbon solvents, as well as in the spectrum of m-nitrophenol solution in the mixture of triethylamine with diethyl ether. In each case, the shift of the equilibrium between the molecular and the ionic types of complexes stops in the temperature range of solvent vitrification where the molecular mobility of the surroundings becomes frozen.

The plot in c_i/c_m vs 1/T for trichlorophenol-trioctylamine system (fig.2) illustrates these results. Here, c_i is the concentration of ionic pairs, c_m

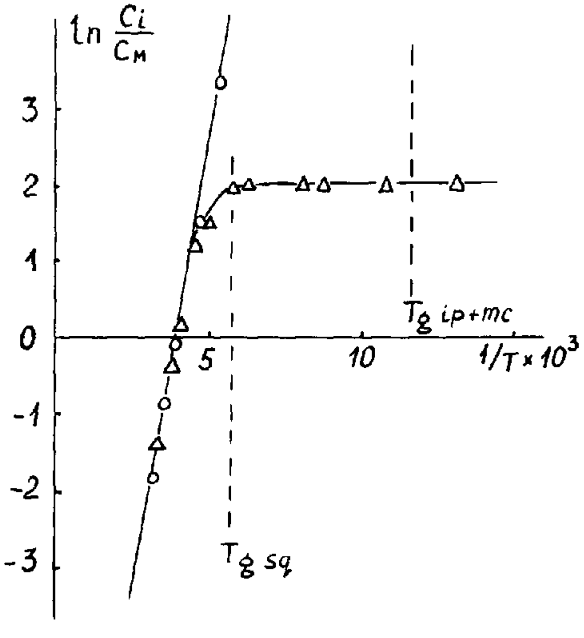
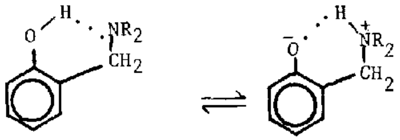


Fig. 2. The dependence of $\ln(c_i/c_m)$ from 1/T for $2,4,5\text{-}Cl_3\text{-}C_6H_2OH + (C_8H_{17})_3N$ complex in squalane (Δ) and in isopentane - methylcyclohexane mixture (o).

is the concentration of molecular complexes. In the region $T > T_g$, when $\tau_s < \tau_e$, the value c_i/c_m represents the equilibrium constant of the monomolecular proton transfer (3). Indeed, the ln c_i/c_m vs 1/T dependence in this region for all the systems studied can be well approximated by the straight line, the parameters of which are the entropy and the enthalpy changes, accompanying the proton transfer in a complex. Near T_g, when τ_s gets measurable with τ_e, the state of the system digresses from the thermodynamic equilibrium, and the considerable deviation from the linear dependence have been observed. At $T<T_g$ ($\tau_s > \tau_e$) the ratio c_i/c_m ceases changing with temperature.

The similar regularities were obtained at spectroscopic investigation of intramolecular proton transfer. The convenient objects were found to be ortho-aminomethylphenols (Mannich's bases). The detailed investigations, carried out in papers {15-17}, had shown, that in solutions of these compounds there exists the tautomeric equilibrium, similar to (3), between the molecular and zwitterionic forms:



(4)

When the temperature decreases, the equilibrium (4) shifts to the right; the independence of the equilibrium position from concentration proves, that the appearance of the ionic form is not connected with self-association. It was found in {17}, that the equilibrium (4) as well as the equlibrium (3) in the case of phenol-amine complexes, gets "frozen" by glassifying of the solvent.

Fig. 3 shows the spectra of solutions of DMT is squalane and in butyl chloride. For both solvents, at sufficient lowering of temperature, one can observe the appearance of the band of the zwitterionic form and the intensity fall of the band of the molecular form of this compound. In both cases these alterations are stopped near the glass transition temperature of the solvent, and the curves of the ln c_i/c_m vs 1/T dependence have a shape, similar to those in fig.2.

Naturally, the value of the ratio c_i/c_m which gets frozen by glassifying of the solvent will depend upon the rate of cooling of the solution (in above described experiments, it was about 1-2 ^{0}/min). However, since near the glass transition temperatures the value τ_s depends strongly on the temperature, the rate of cooling has to be changed appreciably, in order that it should result in the noticeable change of c_i/c_m in a glassified solution. Such rates of

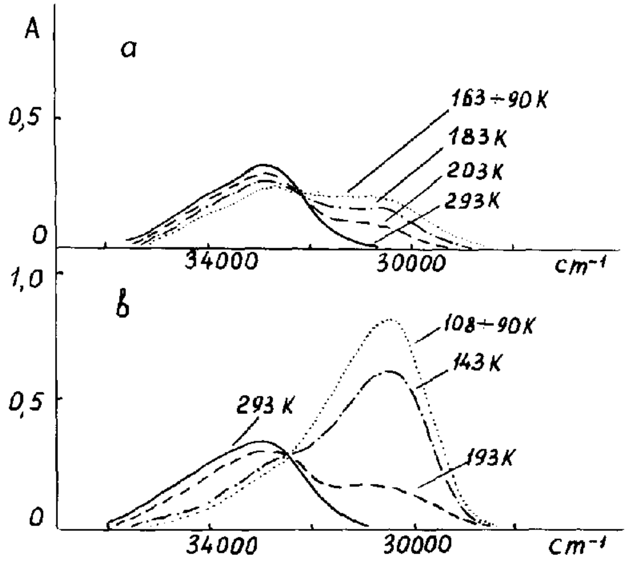


Fig. 3. Absorption spectra of 2-diethylaminomethyl-3,4,5,6-tetrachlorophenol in squalane (a) and in butyl chloride (b) solutions.

cooling are typical for the matrix isolation method, when the sample is deposited on the substrate at the temperature lower than T_g of the solvent. Such experiment was carried out with the system monochloroacetic acid (MCA)-tributylamine (TBA), the latter forming the matrix.

In a liquid solution of MCA in TBA, the equilibrium (3) exists at room temperature; the presence in IR spectrum of the bands 1710 and 1640 cm^{-1} belonging to the C=O group of a strongly hydrogen-bonded MCA molecule and the CO_2^- group of its anion in an ionic pair (fig.4-a) give evidence of it, in accordance with the data {9,18} for such systems. At lowering of the temperature, the equilibrium shifts commonly to the ionic form, so that, below 150 K, the complexes of molecular structure are practically absent in the solution. However, in the matrix prepared at 80 K the situation is quite different. The position of the most intensive band in carbonyl region shows that, in TBA matrix, the majority of complexes MCA-TBA have molecular structure (fig.4-b). A small part of ionic pairs is detected by the shoulder near 1660 cm^{-1}. The shape and the position of the band 1730 cm^{-1} do not differ from those of MCA deposited on the substrate without amine, and its intensity is decreased by dilution. The band of the MCA dimer also has a close frequency.

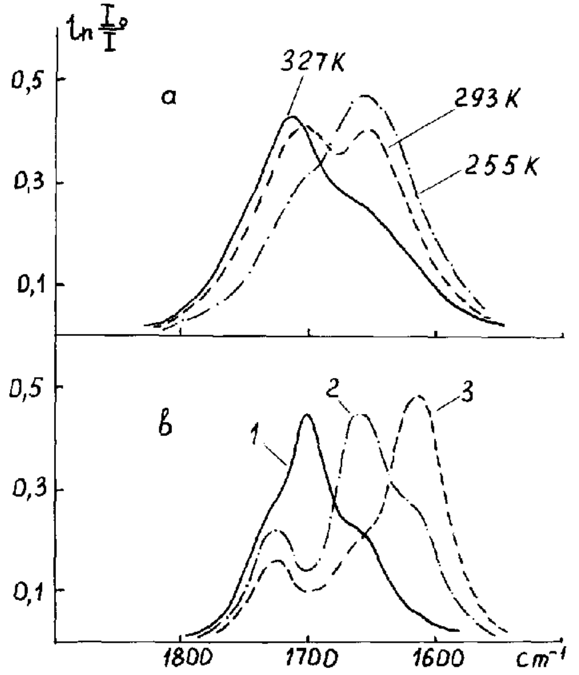


Fig. 4. Absorption spectra of monochloroacetic acid in tributylamine solutions a) liquid solution 0.24 mol/l, d=0.208 mm; b) tributylamine matrix, 80 K, before annealing (1), after annealing during 15 min (2), during 4 hrs (3) at 123 K.

Thus, the band 1730 cm^{-1} can be ascribed to different associates of acid molecules.

Annealing of the matrix at 123 K during 15 min results in full disappearance of the band 1650 cm^{-1}, and increasing the intensity of the band 1650 cm^{-1}, that gives evidence of conversion of molecular complexes to ionic pairs. Simultaneously the band 1615 cm^{-1} appears in the spectrum, which coincides with the band of crystalline salt. In the course of time, its intensity grows slowly on account of the 1650 cm^{-1} band.

Therefore, though at 80 K the ionic form of the complex is more profitable in terms of energy (as it follows from the thermodynamic characteristics of equilibrium (3), at 80 K $\Delta G \simeq 3$ kcal/mol), in the rigid nonannealed matrix, the structure of which is far from the equilibrium, the dominating part of complexes has a molecular form. Only the annealing of the matrix, during which the solvate shell of the complex relaxes to its equilibrium configuration, results in proton transfer and formation of ionic pairs.

DISCUSSION

The experimental data obtained indicate that in systems with equilibria (3) or (4) the proton transfer from one equilibrium state to another occurs as a result of reoganization of the solvate shell of the complex. Since it is correct even for such inert solvents as hydrocarbons, the proton location in the hydrogen bridge has to be very sensitive to the external conditions. In this case the observed structure of the complex in the solution corresponds to such configuration of the molecular environment, when the free energy of the system complex+solvent is minimum. Simultaneous presence of two types of complexes in the solution means, that the free energy of such a system has two minima, corresponding to two different positions of the proton in the hydrogen bridge. However, as it was shown in {20}, the potential energy of the complex under fixed external conditions may possess only one minimum.

The analysis of the connection between the shape of the free energy surface of the system complex+solvent and the shape of the potential surface of the complex was carried out in {20}. It was shown there, that the picture as observed experimentally (i.e. the existence of the equilibrium (3) and its freezing by glassifying of the solution) can take place only if the free energy of solvent structure reorganization accompying the proton transfer, is at least twice more than kT. If the state of the solvent is described by some coordinate, then the condition mentioned above is equivalent to the demand that the change of this coordinate by proton transfer would be twice as much as its mean root square fluctuation. Since the proton transfer is accompanied by substantial (up to 8-10 D) change of dipole moment of the complex, the change of orientational polarization energy of the polar solvent caused by the proton transfer easily answers this demand. In case of nonpolar solvent the reorganization of the environment can be conditioned by anisotropy of polarization of solvent molecules, their quadrupole moment etc. Furthermore, as estimation {20} shows, in case of nonpolar solvent the observed effects can be accounted entirely by changes of the number of solvent molecules in the first coordination shell of the complex.

Summing up, even in nonpolar solvents proton transfer is accompanied by essential reorganization of the solvate shell of the complex, which makes its contribution to the thermodynamic parameters and determines, at least in viscous media, the kinetic parameters of the equilibria with proton transfer.

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