THE EVOLUTION OF THE POTENTIAL SURFACE OF THE REACTION OF CHLOROPHENOLS WITH AMINES

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In the reaction of proton-donor molecules AH and proton-acceptor molecules B in an inert solvent, the complexes formed may have the molecular AH . . . B or the ionic A⁻. . . HB⁺ form. In the present work, using vibrational and electronic spectra, it is proposed to study the equilibria in systems in which the donor are chlorine-substituted phenols and the acceptors are dibutylamine, triethylamine, and pyridine. The main aim of the work was t give the main characteristics of the potential-energy surface for various phenols and to trace the change in the sha of this surface with an increase in the proton-donating capacity of the phenol through the successive introduction o chlorine atoms in various positions of the ring.

The potential energy of the reaction in the proton donor – proton acceptor system AH + B for the simplest ca of a three-atom model depends on three coordinates. Assuming that the minimum energy corresponds to the linea arrangement A H B [1], the potential surface of such a system can be represented by the scheme of Fig. 1a, where and r_2 are the AH and BH distances. In the diagram, one minimum corresponds to a stable complex with a hydrog bond AH . . . B, and the other to a stable ion pair A^- . . . HB^+. Sections of this surface by the planes r_1 = const, r const at great distances give, respectively, the potential curves of the isolated forms BH and AH. The broken line shows the pathway of the system along the two potential surfaces corresponding to the reaction AH + B → A + HB. The possible curves of the dependence of the potential energy of the system on the reaction coordinate Q = Q (r_1, are shown in Fig. 1b. The energy of the system of the noninteracting molecules AH and B was taken as the zero level. The value of ΔE_1 defines the energy consumed in the transfer of a hydrogen atom from a molecule AH to molecule B at great distances, which is large in comparison with the energy of the complexes (for example, for t ClH + NH_3 system it amounts to ≥ 50 kcal/mole [2, 3]). The region of values of Q corresponding to the position the proton approximately in the middle between A and B ($r_1 \approx r_2$) is shown hatched in the figure. The state of th system close to the bottom of the potential trough to the left of this region can be treated as a molecular comple with a hydrogen bond, and to the right of the hatched region are the configurations of a complex in which the pr ton is bound predominantly to the atom B and which correspond to the ion pair A^- . . . HB^+. An experimental cr terion permitting the qualitative characterization of the potential surface of each concrete system may be consic ered to be the form of the equilibria observed in this system. The results obtained in the gas phase, where the di turbing influence of the medium is absent, or in an inert solvent, where it is small, are of the greatest value. In number of cases, the ion pair formed as the result of the transfer of the proton from the donor to the acceptor ca observed spectroscopically in equilibrium with the free molecules. However, the existence of a strong interacti with the molecules of the solvent may lead to a qualitative change in the shape of the potential surface which i shown, for example, in the dissociation of the ion pair into solvated ions. Curves 1 and 2 characterize systems i which there is only one stable complex of the molecular (1) or ionic (2) type, and in case 3 the system has two t of complexes – molecular and ionic – which are in equilibrium. The surface illustrated in Fig. 1a corresponds to this case. The value of ΔE_2 determines the energy of formation of the molecular complex, and ΔE_3 that of the i pair. Curve 1 describes the case found most frequently of a not excessively strong hydrogen bond, which ion pai are not formed in the system. From the results of calculation [4], such systems include, in particular, the dimer of water. A characteristic example of case 2 is the reaction H_3N + HCl → NH_4Cl, which has been investigated oretically and experimentally [5, 6], where the ion pair is present in equilibrium with the free molecules and c plexes with a hydrogen bond do not exist. Finally, curve 3 is typical for the carboxylic acid – amine systems in which the existence of an equilibrium between the molecular complex and the ion pair has been recorded

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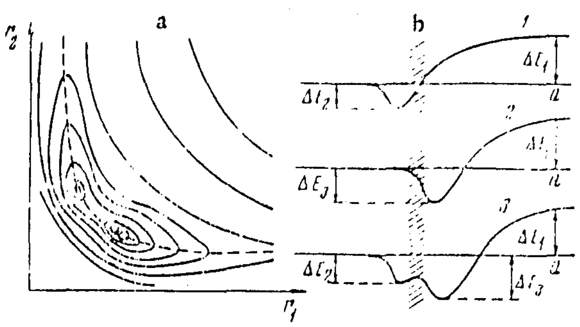

Fig. 1. Potential-energy surface of the AH + B system.

spectroscopically [7]. Measurements of the change in enthalpy in the passage of a proton in the molecular complex have shown that in these systems the potential trough of the ion pair is deeper than the potential trough of the molecular complex [8-10]. Systems also exist the potential curves of which have a minimum in the intermediate region and characterize the so-called symmetrical hydrogen bond [11].

To solve the problem posed, the IR spectra were studied in the 1000-3600 cm^{-1} region (UR-20 instrument) and the UV spectra in the 25,000-40,000 cm^{-1} region (Specord UV-VIS instrument) for the absorption of binary (solution of a phenol in an amine) and ternary (solution of a phenol and an amine in CCl_4 or cyclohexane) systems at temperatures from 10 to 80°C. The interpretation was performed on the basis of the spectra of model systems in which either a complex with a hydrogen bond was formed but there was no transfer of the proton [the acceptor being CH_3CN, $(CH_3)_2SO$, or $(C_4H_9)_3PO$] or the phenol anion was present (metal phenoxides in the solid state and in aqueous or alcoholic solution).

Dibutylamine (DBA). On reaction with DBA, phenol and 4-chlorophenol (4-CP) form only the complex with a OH . . . N hydrogen bond in each case. In the UV spectra of solutions of these phenols in DBA there is a characteristic red shift of the long-wave band of the $\pi \rightarrow \pi^*$ transition by ~ 300 cm^{-1} and of the diffuse vibrational structure, while bands of the ionic forms are absent from the vibrational and electronic spectra. For phenols with a higher proton-donating capacity, in addition to the bands of the molecular complex in the UV spectrum, the appearance of a band shifted in the long-wave direction by 1500-2500 cm^{-1} and possessing no vibrational structure has been recorded, which is typical for the phenoxide ion (Fig. 2a, b). In the IR spectrum there are also bands belonging to the phenoxide ion and to the dibutylammonium cation (in particular, the δNH_2^+ band at about 1630 cm^{-1}). This permits us to speak of the existence of an equilibrium between the two forms of the complex. The relative intensities of the bands of the ion pair and of the molecular complex, which characterize the equilibrium constant of the monomolecular reaction of proton transfer, decrease in the sequence: 2,6-dichlorophenol (DCP); 2,4,5-trichlorophenol (TCP); 2,4-DPC; 3,4,5-TCP; 2-CP; 3,4-DCP. For these phenols, the potential surface of the reaction with DBA has two minima. In all cases, a rise in the temperature leads to an increase in the intensity of the bands of the molecular complex at the expense of the bands of the ion pair and, therefore, the minimum corresponding to the ionic complex on the potential surface is deeper than the minimum corresponding to the complex with a hydrogen bond. It can be seen from Fig. 2b, for example, that in the electronic spectrum of a solution of 2,6-DPC in DBA the band of the molecular complex at about 35,000 cm^{-1} at 12°C is not shown clearly, and it appears in the spectrum only with a rise in the temperature. The opposite pattern is found for 3,4-DPC, in the spectrum of which the band of the ionic complex appears only when the solution is cooled to 7°C. The other phenols mentioned occupy intermediate positions. Finally, for the strongest proton donors, pentachlorophenol (PCP), 2,4,5,6-tetrachlorophenol (TeCP), and 2,4,6-TCP a qualitatively new situation is found. In solutions of the phenols in amines and in ternary systems with an excess of amine a single phenol–amine complex exists which has the ionic structure. When a solution containing comparable concentrations of the donor and acceptor is diluted, bands can be observed in the spectrum that are characteristic for free molecules of the phenol, but it is impossible to detect hydrogen-bond complexes over the whole range of temperatures. This means that the potential surface of the interaction in these systems has a single minimum that is characteristic for the ion pair. The minimum corresponding to the molecular complex is apparently completely absent.

Analysis of the results obtained shows that for phenols with a low-proton-donating capacity the potential surface has one minimum in the region of the coordinates of the hydrogen-bond complex (curve 1, Fig. 1b). With a rise in the proton-donating capacity of the phenol the depth of this minimum increases, and for 3,4-DPC the second potential trough, which is characteristic for an ion pair, appears. This trough has lines deeper than the trough of the molecular complex (curve 3, Fig. 1b), and with a rise in the proton-donating capacity of the phenol the depth of the

"Ionic" trough increases faster than the depth of the trough of the molecular complex. With a sufficiently high proton-donating capacity of the phenol, beginning from 2,4,6-TCP, the first trough disappears and only the one minimum corresponding to the ion pair remains on the potential surface. An increase in the proton-donating capacity of the phenol from 2,4,6-TCP to TeCP and PCP leads to a further increase in the depth of this minimum.

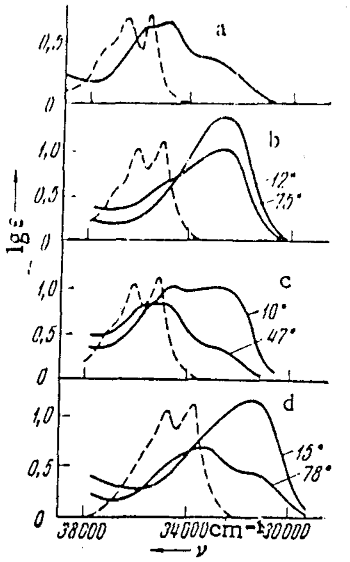

Fig. 2. UV absorption spectra of solutions (~ 10^{-2} M) of chlorophenols in amines (full lines): 2-CP (a), 2,6-DCP (b) in DBA, and 2,6-DCP (c) and 2,4,6-TCP (d) in TEA. The broken lines show the spectra of solutions in C_6H_{12}.

Triethylamine (TEA). The identification of the type of complexes formed by phenols with TEA from their IR spectra, as with other tertiary amines, is complicated by the unfavorable arrangement of the bands of the trialkylammonium cation, while the region of the OH(NH) stretching vibrations proves to be ununiformative. Nevertheless, by combining vibrational and electronic spectra it can be shown that phenol, 4-CP, 3,4-DCP, 2-CP, 3,4,5-TCP, and 2,4-DCP form with TEA only the corresponding molecular complexes, the stability of which rises in this sequence. The bands of the ion pair appear in the spectrum beginning with 2,4,5-TCP and the molecular complex ⇌ ion pair equilibrium shifts to the right successively on passing to 2,6-DCP and 2,4,6-TCP (Fig. 2c, d). At the same time, as in the case of DBA, with an increase in the temperature the concentration of the molecular complexes increases and that of the ion pair falls. For the same three phenols, the potential surface of the interaction with TEA is characterized by curve 3 (Fig. 1b). Only in the case of TCP is it possible to record by means of the electronic and vibrational spectra the existence of an equilibrium of the ion pair with free.molecules and the absence of the molecular complex, which permits us to speak of the absence of a minimum of the molecular complex on the potential surface. The potential surface of the interaction with TEA has form 2 (Fig. 1b) only for the strongest proton donor PCP.

Pyridine. The vibrational spectra of these systems lack the bands of the chlorophenoxide ions and the pyridinium ion and over the whole range the changes typical for a pyridine molecule that take place on the formation of a hydrogen bond – a shift to high frequencies of the bands belonging to the skeletal vibrations, showing a change in the length of the bonds of the C_5H_5N ring – can easily be followed. Similar changes are observed in the bands of the chlorophenols, both in the vibrational and in the electronic spectra. It may be concluded that the interaction of pyridine with chlorophenols does not go further than the formation of the hydrogen-bond complex. No proton transfer is realized in these systems. The interaction of all the phenols with pyridine is characterized by a potential curve of type 1 (Fig. 1b).

Thus, the natures of the changes in the potential surfaces of the interactions of chlorophenols with DBA and with TEA with an increase in the donating-capacity of the phenol are qualitatively similar: for weak proton donors the potential surface has one minimum corresponding to the molecular complex with a OH . . . N hydrogen bond. With an increase in the proton-donating capacity of the phenol a second minimum appears on the potential surface that is characteristic for the stable ionic complex formed in the transfer of a proton via the hydrogen bond to the nitrogen atom. This second minimum always lies below the first. A further rise in the proton-donating capacity of the phenol leads to the disappearance of the minimum corresponding to the molecular complex, and only the single minimum characteristic for the ion pair remains on the potential surface. Consequently, in their proton-donating capacity phenols are precisely the same in their interactions with DBA and with TEA but the passage from one type of potential surface to another takes place for TEA at higher values of the proton-donating capacity than in the case of DBA:

DBA: Ion pair equilibrium MC ⇌ IP MC
PCB > 2,4,6-TCB > 2,6-DCP > 2,4,5-TCP > 2,4-DCP > 3,4,5-TCP > 2-CP > 3,4-DCP > 4-CP > P

TEA: IP equilibrium MC ⇌ IP molecular complex

The arrangement of the phenols in this sequence corresponds to their acidities. In proton-accepting capacity, the secondary amines proves to be more active than the tertiary.

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