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INVESTIGATION OF THE DYNAMICS OF HYDROGEN BONDING IN ORTHO-SUBSTITUTED PHENOLS

G. S. Denisov, N. S. Golubev A. I. Koltsov

Institute of Physics, Leningrad State University, 199164, Leningrad, USSR.
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ABSTRACT

The ^{1}H NMR spectra of phenols with intramolecular hydrogen bonds OH,,,O in solutions containing proton acceptors have been studied in the temperature range (200 to 110)K. The kinetic parameters of the reversible process of intramolecular $\rightleftharpoons$ intermolecular hydrogen bond were determined.

INTRODUCTION

Determination of the life-time of a hydrogen bond by analysis of the full line-shape of the absorption signal obtained by the NMR spectroscopic technique at low temperatures is hindered by the donor's self-association ability leading to the formation of complicated complexes. The life-times of hydrogen-bonded complexes were determined [1,2] in excess of proton acceptor. The other possibility arises when a proton donor with an intramolecular hydrogen bond is used. For instance, ortho-nitro- and ortho-carbonyl-substituted phenols are incapable of self-associating because of the presence of strong intramolecular hydrogen bonds OH,,,O, and the exchange of the OH-protons in these molecules is very slow, so ortho-substituted phenols are convenient for studying the dynamic processes in hydrogen bonding. The kinetics of the dissociation - formation processes of intramolecular hydrogen bonding in symmetrical 2,6-disubstituted phenols have recently been studied [3,4]. At temperatures of 250 K and less proton exchange no longer affects the line shape.

An attempt is made in this study to investigate the interaction between ortho-nitro-, ortho-formyl-, ortho-acetylphenol and the strong proton acceptors 2,4,6-trimethylpyridine (collidine) and hexamethylphosphoroustriamide (hexamethapole). NMR spectra of solutions containing these

compounds at temperatures between (200-110)K were obtained using VARIAN HR 100 and JEOL C 60 spectrometers. The solvents used were CHF_2Cl and a mixture 2:1 of ethylchloride with dichloromethane.

RESULTS AND DISCUSSION

The signal of the OH-group of ortho-nitrophenol on the addition of collidine exhibits a low field shift which increases with temperature decrease (Fig. 1). In the (140-120)K temperature range the signal forms a doublet, the temperature of the splitting depends on concentration of the components. At 110 K the signals are completely separated. The position of the high-field signal coincides with the signal of free nitrophenol. In the presence of excess collidine, only one low-field signal is observed. Thus, there is an equilibrium between free molecules and phenol-collidine complexes having intermolecular hydrogen bonding. Since the relative amount of complexes increases with the decrease of temperature, intermolecular bond is more probable, in terms of energy than intramolecular hydrogen bond-

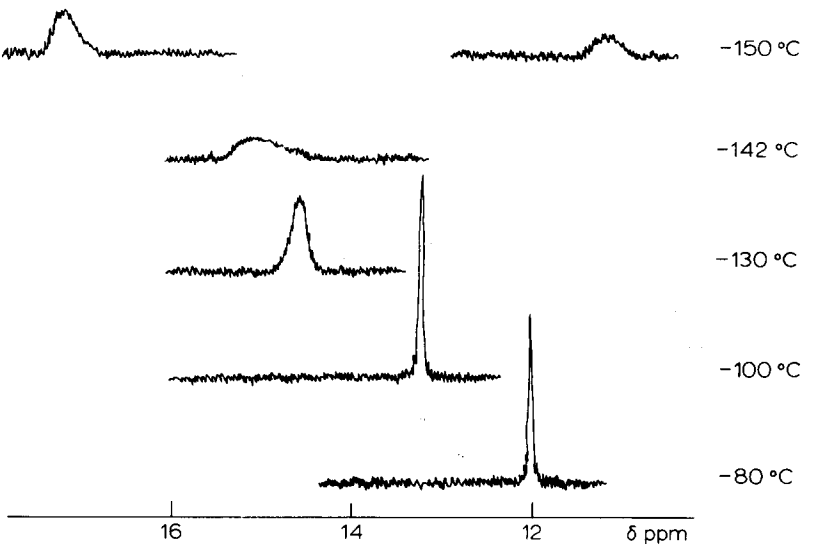


Fig. 1 The spectra of the system o-nitrophenol (0,06 M) + collidine (0,04 M) in CHF_2Cl at various temperatures. At the bottom are spectra of the free o-nitrophenol (δ=10,95 ppm) and of the complex (excess of collidine; δ=17,15 ppm) at 123 K.

ing. In solutions, containing collidine and two different phenols, the OH-signals are seen separately at temperature below 210 K; therefore, below 170 K, the proton exchange will by no means contribute to the averaging of the spectrum. The line shape is determined by the life-time of hydrogen bond. The spectrum of the ortho-nitrophenol - hexamethapole system has principally the same appearance, however, the splitting of the signal occurs at a lower temperature due to a smaller difference in chemical shifts.

Similar changes in spectra with the change of temperature are observed in ortho-formylphenol - collidine and ortho-formylphenol - hexamethapole systems. In this case not only the OH-signal, but also the CHO-signal is split (Fig. 2). The difference between chemical shifts of the CHO-proton

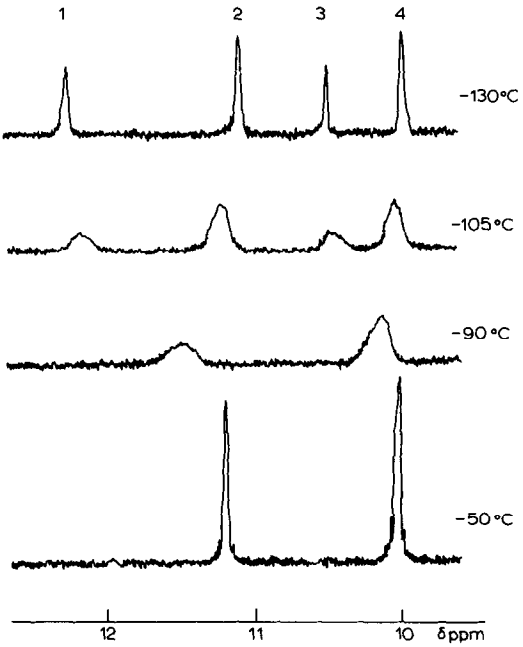


Fig. 2 The spectra of the system o-formylphenol (0,06 M) + hexamethapole (0,04 M) in CHF_2Cl at various temperatures. Signals 1,2 are of OH-group, 3,4 of CHO-group. The signals 1,3 belong to the complex phenol-collidine, 2,4 - to the free phenol molecule.

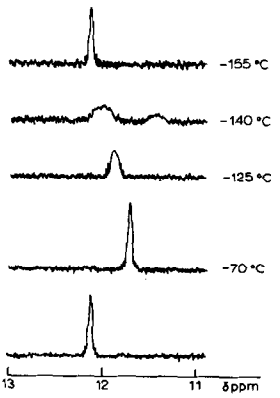
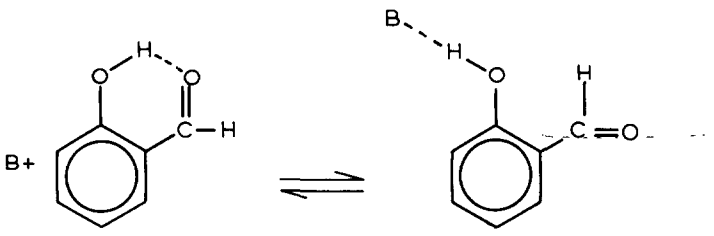


Fig. 3 The spectra of the system o-acetylphenol (0,06M) + hexamethapole (1 M) in CH_2Cl_2/C_2H_5Cl mixture at various temperatures.



(I)

in a free molecule and in complexes may be explained by the different orientations of this group relative to OH-group [4,5]:

The intramolecular hydrogen bond in ortho-acetylphenol is very strong. No change is observed at different concentrations or temperatures, in the spectra of solutions containing ortho-acetylphenol and collidine or hexamethapole in CHF_2Cl solvent compared with the spectrum of free acetylphenol. However, if a mixture of ethylchloride with dichloromethane is used as a solvent then, in the case of excess hexamethapole (10-15 times), one can see the high field shift of the OH-signal. On decreasing the temperature the chemical shift of this signal approaches the value typical for the free ortho-acetylphenol, and later the signal splits (see Fig. 3; the spectrum of the free phenol is given at the bottom). Further the high field signal belonging to the complex with the intermolecular hydrogen bond disappears. Therefore, in this case the species with intramolecular hydrogen bonding is more likely in terms of energy. It should be noted that at room temperature the complex of ortho-acetylphenol with hexamethapole in free hexamethapole used as a solvent may be detected by the infra-red absorption spectra. In these spectra there are two bands in the CO group stretching vibration region. One of them is of the free CO group in the complex with hexamethapole, the other is of absorption of CO-group involved in intramolecular hydrogen bond with OH-group (1661 and 1636 cm^{-1}). It is interesting to note, that the relative quantity of free molecules increases with increased temperature; hence, in pure hexamethapole, the species with intermolecular hydrogen bonding is more likely in energy terms, because of the stabilization of a more polar form in a more polar solvent. Complexes of ortho-acetylphenol with collidine as well as with other acceptors (dimethylsulfoxide, dimethylformamide) were not formed.

To obtain quantitative data, the spectra of several (5-8) initial con-

centrations of the compounds considered were taken in the interval 0,02-0,3 M. From these spectra, the relative quantities of species with intra- and intermolecular hydrogen bond were determined. For cases of rapid exchange, the determination was made using the position of the averaged signal; while, for slow exchange the relative integrated intensity of the signals of the two species was used. In view of the fact, that the temperature regions of intermediate exchange in the spectra, obtained for two frequencies (60 and 100 MHz) do not overlap, determination of relative concentrations is possible within the whole temperature range (220 to 120) K. The life-times of the species were found by building theoretical line-shapes, using procedure [6] on M-222 computer, and the necessary population densities for particular temperatures were calculated [6]. The line-width in case of no exchange was measured in the spectra of solutions containing the phenol only.

For ortho-formylphenol, the life-times of the forms, defined from the OH- and CHO-signals, coincide. Since the intermolecular proton exchange may affect the averaging of the OH-signal, and does not affect the averaging of the CHO-signal, this coincidence proves that the rate of the proton exchange is small compared to the rate of the process (1). The phenol added to the solution at temperatures below 220 K, gives a narrow signal, the shapes of aldehyde signals remain unchanged. The life-times of the complexes were not found to depend on the initial component concentrations. Hence, the transition of the species from an intermolecular to an intramolecular hydrogen bond is of monomolecular character. From the temperature dependence of the rate constants of the forward and backward reactions (200 to 130) K and of the equilibrium constant (250 to 120) K, thermodynamic and kinetic parameters of the processes (1) were determined (Table 1).

The high values of activation enthalpy leads us to assume that the processes are accomplished step by step, through breaking of one and formation of the other hydrogen bond. The values of activation entropy indicate that there is practically no intermolecular hydrogen bonding in the transition state. The path's profile of such a process has the shape shown in Fig. 4. The depth of the potential well of state II, which can not be detected spectroscopically because of its poor population, is supposed to be dependent on the activation energy of the diffusion in the solution.

TABLE 1

THE ENTHALPY CHANGE ΔH, THE ACTIVATION ENTHALPY $E^{\ddagger}$ AND ENTROPY $\Delta S^{\ddagger}$ OF THE FORWARD AND BACKWARD REACTION (I)

PHENOL+ACCEPTOR	$-\Delta H$ Kcal/mole	$E_b^{\ddagger}$ Kcal/mole	$E_f^{\ddagger}$ Kcal/mole	$\Delta S_b^{\ddagger}$ e.u.	$\Delta S_f^{\ddagger}$ e.u.
1. 2-NITROPHENOL+COLLIDINE	6.0±0.3	13.2±0.6	6.8±0.6	+20	+6
2. 2-NITROPHENOL+HEXAMETHAPOLE	5.1±0.3	11.9±0.6	6.7±0.6	+19	+6
3. 2-FORMYLPHENOL+COLLIDINE	5.0±0.3	12.8±0.6	8.0±0.5	+17	+2.5
4. 2-FORMYLPHENOL+HEXAMETHAPOLE	3.2±0.3	11.4±0.7	8.1±0.6	+16	+2.3
5. 2-ACETYLPHENOL+HEXAMETHAPOLE	-0.3±0.1	10.6±0.6	10.8±0.6	+19	+5

(1-4 IN CHF_2Cl, 5- IN MIXTURE $C_2H_5Cl + CH_2Cl_2$

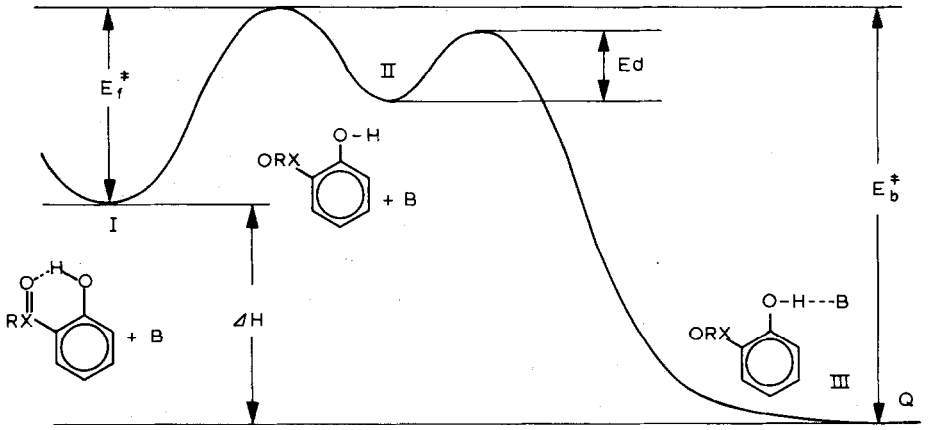


Fig. 4 The reaction path profile of the formation of complex with intermolecular hydrogen bond by ortho-substituted phenols.

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