



“Additive” cooperativity of hydrogen bonds in complexes of catechol with proton acceptors in the gas phase: FTIR spectroscopy and quantum chemical calculations

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ABSTRACT

Experimental study of hydrogen bond cooperativity in hetero-complexes in the gas phase was carried out by IR-spectroscopy method. Stretching vibration frequencies of O–H groups in phenol and catechol molecules as well as of their complexes with nitriles and ethers were determined in the gas phase using a specially designed cell. O–H groups experimental frequency shifts in the complexes of catechol induced by the formation of intermolecular hydrogen bonds are significantly higher than in the complexes of phenol due to the hydrogen bond cooperativity. It was shown that the cooperativity factors of hydrogen bonds in the complexes of catechol with nitriles and ethers in the gas phase are approximately the same. Quantum chemical calculations of the studied systems have been performed using density functional theory (DFT) methods. It was shown, that theoretically obtained cooperativity factors of hydrogen bonds in the complexes of catechol with proton acceptors are in good agreement with experimental values. Cooperative effects lead to a strengthening of intermolecular hydrogen bonds in the complexes of catechol on about 30%, despite the significant difference in the proton acceptor ability of the bases. The analysis within quantum theory of atoms in molecules was carried out for the explanation of this fact.

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1. Introduction

Among all types of non-covalent interactions, formed in organic molecules, hydrogen bonds have the greatest impact on their properties and reactivity [1–3]. Cooperativity is an important property of hydrogen bonds. The cooperativity means strengthening or weakening of the hydrogen bonds in the complexes with the adjacent hydrogen bonds in comparison with the binary complexes with a single one [2,4–6]. Cooperativity of hydrogen bonds determines the structure and properties of self-associated solvents (water, alcohols, amides, etc.) [7–10]. In addition, cooperative effect of H-bonding leads to additional stabilization of supramolecular architectures [11,12], proteins and nucleic acids [13,14]. One of the most suitable methods to study the cooperativity of hydrogen bonds is IR spectroscopy. This method was used for the investigation of cooperative effects in multi-particle complexes formed in solution [15] and in the inert gas matrices [16]. Study of the cooperative effects in condensed matter is complicated by the presence of various types of non-covalent interactions and the solvent effects [17]. Therefore, investigation of hydrogen bonds cooperativity in the gas phase is of great interest. These studies can give the opportunity to quantify “neat” cooperative effect and to understand the

nature of H-bond cooperativity phenomenon. Experimentally the cooperative hydrogen bonds in the gas phase were studied only in clusters of aliphatic alcohols and water. The main results of these investigations were reviewed in [18]. The authors [18,19] using IR-spectroscopy method showed that the strength of hydrogen bonds in clusters of alcohols and water is much greater than in dimers. Experimental studies of the hydrogen bond cooperativity in complexes consisting of different molecules were not carried out in the gas phase. In the last decade, the cooperativity of hydrogen bonds in the gas phase was mostly studied using various quantum chemical approaches. Theoretical calculations provide an opportunity to study systems with cooperative hydrogen bonds, consisting of different number of molecules, which are very difficult to study experimentally. Hydrogen bond cooperativity in clusters of amides [6,20], some biological molecules [21] and in systems with multiple unusual weak hydrogen bonds [22] was studied using different quantum-chemical methods. Authors [23] also used quantum theory of atoms in molecules (QTAIM) approaches for analysis of this phenomenon. In works [24,25] calculations of intramolecular hydrogen bond cooperativity were carried out. Despite significant progress in the use of theoretical calculations, experimental studies of hydrogen bond cooperativity in the gas phase are rather poorly distributed.

In this work, we have carried out the experimental study of hydrogen bond cooperativity in the gas phase using the infrared spectroscopy method. It is quite difficult task to determine spectral

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parameters of ternary hetero-complexes with adjacent hydrogen bonds in the gas phase. Therefore, we examined the complexes consisting of two molecules, one of which forms an intramolecular hydrogen bond. Complexes of catechol with different proton acceptors were used as objects of investigation. Catechol is a polyhydroxy organic compound, which is widely used in industry. It is able to form adjacent hydrogen bonds with proton acceptors that can significantly affect its reactivity and antioxidant capacity [26–28]. Earlier complexes of catechol with proton acceptors were investigated in the liquid state [26,27,29]. In this paper we study them in the gas phase and analyze the effect of proton acceptors on the value of cooperative effect. Theoretical calculations were carried out for the validation of the new experimental results. Geometrical, spectroscopic and energetic parameters of studied complexes were calculated using the DFT methods. The nature of cooperative effect was discussed using QTAIM analysis.

2. Experimental

Samples of phenol and catechol were purchased from Aldrich with a mass-fraction purity of about 0.99. Before experiments they were additionally purified. Catechol was recrystallized in benzene. Additionally it was purified by repeated fractional sublimation under reduced pressure. Analytical grade phenol has water as its main impurity. Therefore, phenol was dried by distillation from a benzene solution to remove the water-benzene azeotrope and the excess benzene, followed by distillation of the phenol at reduced pressure. All purification procedures were performed in a nitrogen atmosphere. The degree of purity was controlled by gas chromatography. The lack of oxidation of the studied phenols in the presence of organic substances was checked by IR spectroscopy.

Nitriles and ethers used in IR measurements were analytical grade (Aldrich, 99%). They were dried and distilled before use by standard methods [30]. Nitriles were shaken with Linde 4A molecular sieves. Subsequently they were stirred with calcium hydride until no further hydrogen is evolved. The nitriles were then fractionally distilled over P_2O_5 to remove most of the remaining water. Traces of P_2O_5 were removed by distilling from anhydrous potassium carbonate. Ethers were refluxed with and distilled from $LiAlH_4$ to remove water, peroxides and other impurities. After they were additionally dried and fractionally distilled from sodium. Residual water content in nitriles and ethers was checked by Karl Fischer titration and IR spectroscopic measurements. It does not exceed 5×10^{-3} volume percent for the studied chemicals.

The infrared spectra were received using the FTIR Bruker Vector-22 spectrometer ($400\text{--}4000\text{ cm}^{-1}$) equipped with a global source, a KBr beamsplitter and MCT (mercury cadmium telluride) detector. The interferograms were recorded with a resolution of 2 cm^{-1} and Fourier transformed using a Blackman-Harris apodization function. The number of scans used in a particular experiment was 64.

The gas phase experiments were performed exploiting hand made glass cell, similar enough to use by Lin and Fishman [31]. The sample path length for all experiments was 10 cm. The cell windows were 32 mm diameter CaF_2 disks. Spectra were obtained under inert N_2 atmosphere. Temperature was measured by the thermocouple and was kept constant using the power supply with adjustable voltage to ensure a standard deviation smaller than 1 K.

Experiments in vapor phase included the measurements of the IR-spectra of pure phenols, proton acceptors and their mixtures, respectively, at the same temperature. Weight of sample of studied substances, placed in a cuvette for measurement, was always the same and equal to 50 mg. The interactive spectral subtraction was performed for the determination of H-bonded O–H group vibration frequencies in complexes $ROH \cdots B$. The spectra of pure base and phenol or catechol were subtracted from the spectra of their

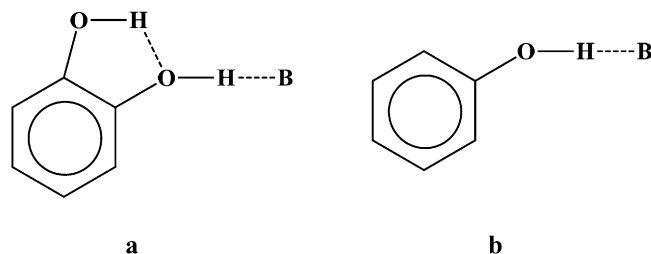


Fig. 1. Studied complexes of catechol (a) and phenol (b) with proton acceptors (B).

mixtures. The position of the absorption band (in cm^{-1}) was found as the abscissa of the experimental contour maximum. Thus, an experimental contour was wide, first-order derivatives were used for location the maximum.

3. Computational details

Quantum chemical calculations of catechol and phenol molecules, as well as of its complexes were carried out in Firefly package [32] using B3LYP hybrid DFT functional [33], which combines Becke's three-parameter functional [34] with the non-local correlation provided by the correlation functional of Lee et al. [35] and VWN formula 1 [36] RPA correlation (as in Gaussian and NWChem but GAMESS packages). It is well-known fact that the DFT methods require a moderate expense of time and provide good results for normal stretching vibration frequencies of molecules [37]. Pople's basis set 6-311++G(d,p) of triple-zeta quality for valence shell with diffuse and polarization functions on all atoms was used for calculation. High quadratures with 155 radial points and 590 Lebedev angular grid points were used. Tight SCF criteria was applied to get accurate vibration frequencies. It was found in our tests (see Table S1 of supporting materials) that the results obtained with chosen basis set do not differ significantly from those obtained by using extremely precise calculation with basis set 6-311++G(3df,3dp) and "army-grade" quadratures (200 radial points and 2090 Lebedev angular grid points). Basis set 6-311++G(d,p) provides very small BSSE error (less than 0.5 kcal/mol). The structure of all the molecules and complexes was obtained by complete optimization of geometry. The optimized structures belong to the minimum of potential energy surface, which was verified by calculating the second derivatives matrix (Hessian), all of whose members had a positive value. The magnitude of the superposition error slightly changes in going from one complex to another (less than 0.1 kcal/mol in most cases). Thermodynamic functions were calculated with the inclusion of BSSE correction (see Table S1).

The calculations of topological characteristics of the electron distribution in molecules as well as integrated atomic characteristics within quantum theory of atoms in molecules (QTAIM) [38] approaches were carried out on AIMAll Professional package [39]. All discussed QTAIM-properties are in atomic units (the list of atomic units and transition coefficients are in Table S2 of supporting material).

4. Results and discussion

4.1. IR-spectroscopy

We have studied cooperative hydrogen bonding of catechol with proton acceptors in gas phase using IR-spectroscopy method. Catechol forms complexes with the adjacent hydrogen bonds with an equimolar amount of base (B) (Fig. 1). In such complexes the inter- and intramolecular hydrogen bonds influence on the strength of each other (cooperative effect) as was shown in [25–27,29].

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