

The structure of phenol–ammonia clusters before and after proton transfer. A theoretical investigation

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Abstract

Equilibrium structures are reported for clusters of phenol with up to five ammonia molecules at the Hartree–Fock level of theory with checks based on Møller–Plesset and density-functional methods. A systematic build-up of solvent shells is observed. For the clusters with five ammonias a metastable ion-pair structure is obtained. The results are related to the observed proton-transfer dynamics in electronically excited clusters. © 1997 Published by Elsevier Science B.V.

1. Introduction

Most chemical processes of practical and biological interest take place in solution with the solvent serving not only to disperse the reactants but also to provide specific solvation to reactants and products. While the influence of solvents on reactivity has been recognized for a very long time, detailed information on the local structure of solvated reactants or products is scarce. For obvious reasons it is difficult to isolate these structures within the bulk of a solution. Yet such information might allow us to achieve greater control over chemical processes through the selection of appropriate solvents and reaction conditions. For instance, in the case of electron transfer in polar solvents, it has been found that up to two-thirds of the reorganization energy of the solvent is due to the first two solvation layers [1].

One way to avoid the complexity inherent in bulk systems is to focus on small clusters of reactants and solvent molecules. Such clusters can be prepared in cold expansion beams and studied by high resolution techniques. They are also amenable to high-level theoretical calculations. Once a detailed picture is obtained of the reaction in a small cluster, several avenues are open to generalize the results to bulk systems, two of the more promising being to increase the cluster size and to extend the study to reactions in solid matrices.

In a recent review, Syage [2] has discussed several solvent-assisted reactions observed in clusters, his main focus being on proton transfer in clusters of phenol and naphthol with up to five ammonia molecules. No reaction is seen in the electronic ground state of the phenols, but in the first excited singlet state proton transfer to an ammonia molecule occurs, once a critical minimum number of ammonia molecules is present, namely three for naphthol [3–6] and five for phenol [7–18]. Since the excited phenols are much stronger

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acids than their ground-state equivalents [19,20], it is not surprising that the transfer requires electronic excitation. The time dependence of the transfer has been measured as well [3–7,13,14,17,18], and found to be given by a time constant of about 60 ps. The transfer is followed by a slower process, dependent on excitation energy and cluster size, and therefore ascribed to solvent reorganization.

Attempts to derive the cluster structure from spectroscopic observations have thus far been successful only for the smallest clusters [21–23]. Structural information on the clusters in which the transfer takes place remains scanty [23]. Given the large number of low-frequency vibrations in these clusters, extraction of structural data from rotational fine structure will be exceedingly difficult. For these reasons we are undertaking a series of ab initio calculations in order to supplement the experimental data with theoretical results. Very few calculations of this type are available to date [24]. While it is our ultimate aim to relate the structure before and after proton transfer to the transfer rate, we restrict ourselves in this preliminary report to the structure of clusters of ground-state phenol with up to five ammonia molecules before and after proton transfer, whenever such a transfer leads to a metastable structure. Although no proton transfer is observed in cold ground-state clusters, our preliminary results on excited-state clusters indicate that the main effect of excitation of phenol to the first excited singlet state is tightening of the structure without altering the molecular arrangement. Therefore we expect the ground-state results reported here to be directly relevant to proton transfer in the excited state.

2. Calculations

Calculations of the equilibrium structure and vibrational force field of clusters of ground-state phenol with up to five ammonia molecules were carried out at the HF/6-31G* level. To probe the dependence of the results on electron correlation additional calculations were carried out at the MP2/6-31G* level (up to $n = 3$) and the DFT-BLYP/6-31G* level (up to $n = 4$). In all cases these calculations confirmed the solvent arrangements obtained at the Hartree–Fock level, the main difference being tightening of the hydrogen bonds in the order DFT > MP2 > HF. We therefore

assume that the reported structures give realistic pictures of the clusters, the main uncertainty being the exact values of the interatomic distances and the corresponding frequencies. These structures, obtained with the Gaussian 94 suite of programs [25], are illustrated in Figs. 1–4 and Table 1.

A clear pattern of solvation emerges from these results. The first ammonia molecule, to be labeled α -NH₃, forms a nearly linear hydrogen bond of the type N...HO with the hydroxyl group, in agreement with spectroscopic observations on naphthol [22]. The second ammonia molecule, β -NH₃, forms two hydrogen bonds, an NH...O bond with phenol and an N...HN bond with α -NH₃, in a strained triangular arrangement with three bent hydrogen bonds illustrated in Fig. 1. The third ammonia molecule, γ -NH₃, inserts itself between α - and β -NH₃, forming an N...HN and an NH...N bond, respectively. The resulting square, planar arrangement characterized by nearly linear hydrogen bonds is illustrated in Fig. 2. It constitutes the first solvent shell and remains intact upon the addition of further ammonia molecules. The next pair, δ -NH₃ and ϵ -NH₃, forms N...HN type hydrogen bonds with α -NH₃, assuming nearly symmetric positions above and below the plane of the phenyl ring and the first solvent shell, as illustrated in Fig. 3. We speculate that the subsequent pair of ammonia molecules will solvate β -NH₃, to be followed by a pair solvating γ -NH₃ and thus completing the second solvent shell.

It follows from Table 1 that the gradual addition of ammonia molecules leads to a corresponding strengthening of the original α -N...HO bond, as evidenced by the shortening of the α -NO distance and the lengthening of the HO bond. The frequency of the α -N...HO stretching vibration changes accordingly from 155[202] cm⁻¹ for $n = 1$ to 171[224] cm⁻¹ for $n = 2$, to 181[259] cm⁻¹ for $n = 3$, to 195[278] cm⁻¹ for $n = 4$ and to 229 cm⁻¹ for $n = 5$ (the numbers in square brackets refer to DFT calculations). These gradual changes prepare the way for the transfer of the proton whereupon the α -NH...O stretching vibration acquires a frequency of 291 cm⁻¹. In the ground state, the $n = 5$ cluster with a transferred proton is calculated to be endothermic by 2140 cm⁻¹. Its metastable structure, depicted in Fig. 4, is quite different from that of the stable $n = 5$ cluster shown in Fig. 3. The first solvent shell can still be recognized but has moved out of the plane of the phenyl ring,

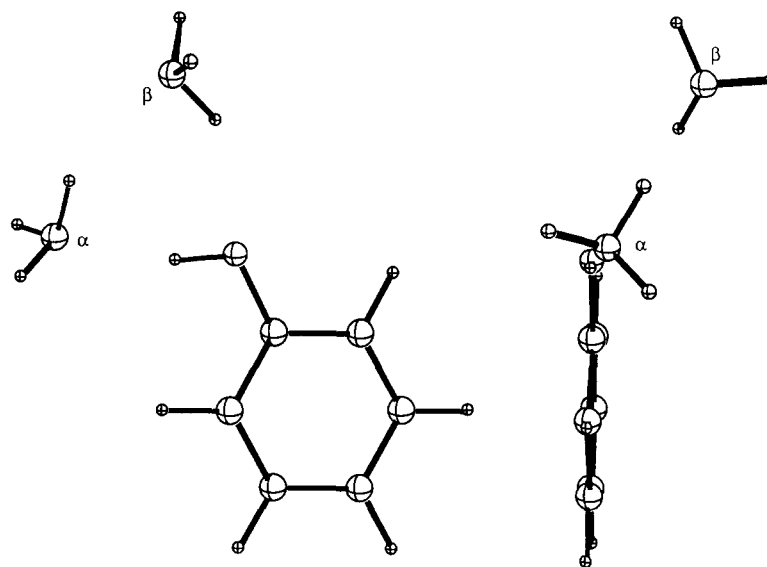


Fig. 1. Two projections of the equilibrium structure of phenol.(NH₃)₂ cluster calculated at the HF/6-31G* level. Calculations at the MP2 and BLYP-DFT levels show the same molecular arrangement but slightly shorter intermolecular distances (see Table 1).

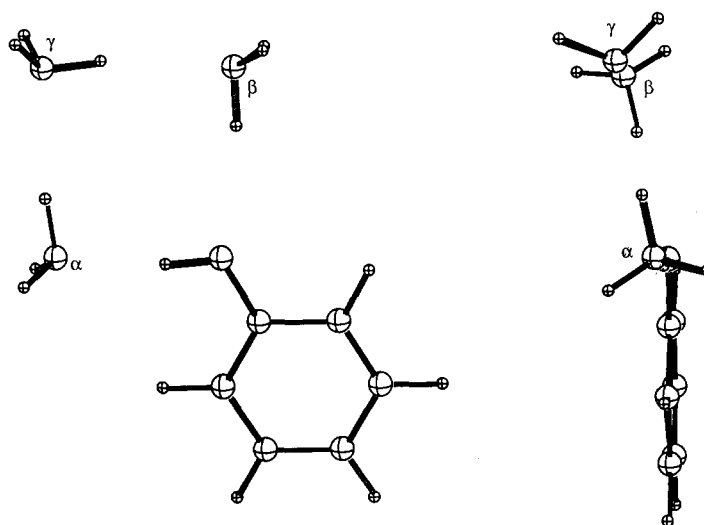


Fig. 2. Same as Fig. 1 for phenol.(NH₃)₃.

apparently to make room for an additional O...HN bond with δ -NH₃ which now solvates both α -NH₄⁺ and the phenolate ion. In this arrangement the overlap between the lone-pair electrons of the oxygen and the π -electrons of the phenyl ring is not maximal, since the strongest O...HN bond, namely that with α -NH₄⁺,

is no longer situated in the plane of the ring. Apparently this loss is overcompensated by the gain resulting from the additional hydrogen bond. No metastable structures with a transferred proton were found for $n \leq 4$, either at the HF or the DFT level. In all these cases the structures reverted to those in the table.

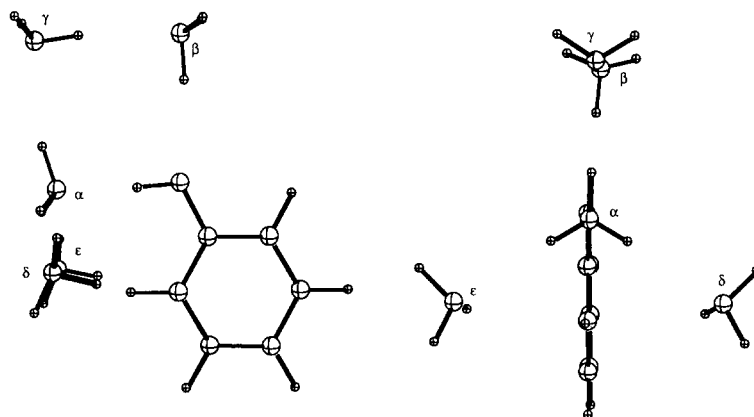


Fig. 3. Two projections of the equilibrium structure of phenol.(NH₃)₅ cluster calculated at the HF/6-31G* level.

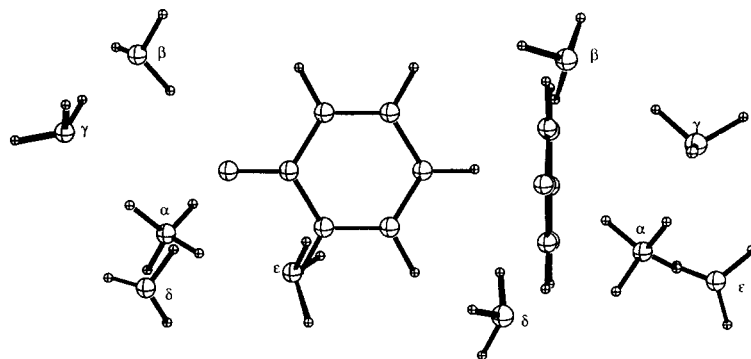


Fig. 4. Two projections of the metastable structure of the ammonium phenolate.(NH₃)₄ cluster calculated at the HF/6-31G* level. Its energy exceeds that of the structure in Fig. 3 by 2140 cm⁻¹.

3. Discussion

The calculations indicate that, in cold beams, phenol–ammonia clusters, PhOH.(NH₃)_n, have, for small *n*, well-defined equilibrium structures due to the strength and the specificity of the hydrogen bonding. The ammonia molecules are arranged in recognizable shells of which at least the first tends to be persistent. As shown above, the observed structures are readily interpreted in qualitative terms. Thus the following simple rules seem to govern the build-up of a solvation layer: (i) the first solvent molecule attaches itself so as to form the shortest possible hydrogen bond which in general will involve the proton most apt to transfer; (ii) subsequent solvent molecules attach themselves to the reactive site until electronic or

steric saturation is achieved and also to the primary solvent molecule to form loops of minimal strain, i.e., with hydrogen bonds as linear as the structure allows; (iii) for hydrogen bonds between two solvent molecules, the one with the strongest bond to a third molecule donates the hydrogen; (iv) if the reactive site is saturated the next solvent molecule attaches itself to the solvent molecule engaged in the strongest hydrogen bonding; (v) the solvent loops are oriented so as to maximize the bonding between the reactive site and the rest of the molecule, if the available space allows such an arrangement.

With these tentative rules one can readily construct two solvent layers. It is likely that subsequent layers will form structures close to those characteristic of the neat solvent. Also, with increasing cluster size one ex-

Table 1

Separation of hydrogen-bonded atoms (in Å) and deviations from linearity of the corresponding hydrogen bonds (in degrees) in phenol-(NH₃)_n and ammonium phenolate-(NH₃)_m complexes, calculated, respectively, at the levels HF, MP2 (in parentheses) and DFT-BLYP (in square brackets) with the 6-31G* basis set

Bond	<i>n</i> = 1	<i>n</i> = 2	<i>n</i> = 3	<i>n</i> = 4	<i>n</i> = 5	<i>m</i> = 4
H...O	0.959 ^a /— (0.993/—) [1.008/—]	0.963/— (1.003/—) [1.023/—]	0.966/— (1.011/—) [1.039/—]	0.972/— [1.076/—]	0.978/—	1.596/—
αN...O	2.945/9.9 ^b (2.860/8.4) [2.828/10.8]	2.881/16.9 (2.777/17.5) [2.735/19.4]	2.866/9.7 (2.749/10.1) [2.705/11.3]	2.824/9.6 [2.626/10.7]	2.787/ 3.9	2.644/9.1
βN...O		3.299/32.7 (3.150/30.4) [3.143/33.1]	3.236/9.5 (3.080/10.0) [3.078/12.6]	3.251/6.8 [3.071/9.3]	3.248/7.5	3.062/8.6
δN...O						3.129/27.4
αN...βN		3.210/20.8 (3.058/22.3) [3.008/21.7]				
αN...γN			3.201/7.9 (3.051/9.8) [2.984/10.1]	3.263/10.6 [3.023/12.1]	3.296/15.3	2.985/14.6
αN...δN				3.334/23.4 [3.115/19.9]	3.377/29.4	2.989/27.0
αN...εN					3.385/28.5	3.031/11.7
βN...γN			3.296/9.5 (3.130/9.0) [3.056/12.6]	3.295/9.0 [3.076/12.8]	3.326/28.5	3.183/14.8

^a Separation.

^b 180° – (hydrogen-bond angle).

pects alternative, metastable structures to become significant and to dominate the behavior at higher temperatures. This aspect remains outside the scope of the present study.

Thus far a metastable structure for solvated ammonium-phenolate has been found for only one cluster, namely PhO[−]NH₄⁺(NH₃)₄. Hence in this case there is no clear picture of how the solvent shell is formed. The calculated structure is characterized by a trade-off between maximal π-electron overlap and maximal hydrogen bonding. Therefore it seems possible that the addition of more ammonia molecules may alter the structure of the solvent shell and give rise to a significant further stabilization of the ion-pair cluster

relative to its nonionic parent. This aspect remains to be investigated both experimentally and theoretically. If we assume that the calculated structures for the ion-pair cluster and its nonionic parent are also representative of the corresponding excited state clusters, an assumption supported by preliminary calculations, then we can draw the following qualitative scenario of the proton-transfer reaction. Upon excitation, the PhOH.(NH₃)₅ cluster tightens but retains its basic shape, while becoming metastable with respect to proton transfer. To form the equilibrium structure after transfer, large displacements of the nitrogen atoms are required, so that the Franck–Condon factors for direct transfer between the two equilibrium configura-

tions will be very unfavorable. Therefore transfer will initially produce a structure resembling that of the nonionic cluster with relatively minor displacements of the nitrogen atoms. Such a transfer is feasible only when the overall transfer process is sufficiently exothermic. The observed slow solvent relaxation following fast proton transfer [3,7,8,13–18] is in agreement with this picture. Generating a quantitative description of these processes is a challenge that will be addressed in future publications. However, the structural information provided by the calculations offers a rational basis for a qualitative understanding of the proton-transfer dynamics in these clusters.

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