The Structure of DMF · HCl and DMF · (HCl)₂ Complexes according to *ab initio* Calculations

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Abstract—Based on *ab initio* calculation at the 6-31G level, the differences in the structures of isolated complexes of DMF with HCl with compositions 1 : 1 and 1 : 2 are analyzed. The interaction of HCl with DMF results in the formation of the molecular complex. When HCl is added to this complex, a proton transfers to the DMF molecule and the asymmetric fragment Cl···HCl is formed. Calculated data are compared with the structures of DMF complexes with HCl in the condensed phase.

INTRODUCTION

The catalytic properties of acid solutions are largely determined by the presence of acid–base complexes and ions formed by strong hydrogen bonds [1, 2]. Depending on the depth of the acid–base interaction between the acid (HA) and the solvent (B), molecular complexes, ionic pairs, and ions [3], as well as uncharged complexes with incomplete proton transfer to the base molecule (quasi-ionic pairs) [4, 5], can be formed. In solutions with excess acid anions, (AHA)⁻ can be formed with strong symmetric hydrogen bonds [4, 6].

Molecular complexes AH···B, quasi-ionic pairs A···H···B, ionic pairs A⁻···HB⁺, and anions (A···H···A)⁻ have different catalytic activities. That is, they possess different abilities to convert organic compounds into the ionized form in the acid solution [2]. In other words, the catalytic activity of an acid–base complex is associated with the degree of proton transfer from the acid molecule to the base molecule. The identification of acid–base complexes with different structures using vibrational spectra is possible [7], because the characteristic absorption in the IR spectra of such complexes depends on the degree of proton transfer.

In solutions of strong acids in aprotic solvents, positively charged double solvates of proton analogous to the ions $H_5O_2^+$ and $(H_2O···H···OH_2)^+$ are practically not formed [1, 6]. Without determining the structures of acid–base complexes and the degree of proton transfer, it is impossible to judge the mechanism of the catalytic action of acid solutions. The identification of acid–base complexes according to spectral data is based on the semiempirical theory of vibrational spectra of the systems with hydrogen bonds [8]. This theory explained the nature of the continuous absorption of the double solvates of proton with symmetric and quasi-symmetric hydrogen bridges. This theory also enabled the quanti-

tative comparison of calculated and experimental IR spectra of such double solvates and made it possible to obtain their acceptable agreement, as well as to predict the effects of temperature and solvation.

At the same time, theoretical estimates of the geometric parameters and the distribution of charges in acid–base complexes in solutions have not been obtained until recently for the following reasons. In acid solutions, ions and complexes are strongly solvated. Therefore, in the calculation of geometries and charges at atoms, it is virtually impossible to take into account all the interactions between species. On the other hand, it is the molecular environment of an acid–base complex that stimulates the transfer of a proton from an acid to a base [9]. Direct measurements of geometric parameters are only possible in the crystal phase using diffraction methods, but the results of such measurements may not reproduce the situation in the liquid phase. Available literature data on the structure and distribution of charges primarily refer to isolated complexes, and these calculations can only be compared with experimental results in the gas phase. Both calculated and experimental data show that, in the interaction of acid and base molecules in the gas phase, only molecular complexes are formed and proton transfer is not observed [9, 10].

The goal of this work is to determine the structure of the acid–base (1 : 1) complex using *ab initio* calculation and measure the geometric parameters and charges at atoms in its interaction with an acid molecule. Finding a solution to this problem is important for understanding the processes of solvation of acid–base complexes in the concentrated solutions of acids and for determining the relationship between the activity of these complexes and their solvation in the solutions of acids with a high concentration of inert solvents. It is known [11] that inert solvents considerably affect the acidity function of a solution.
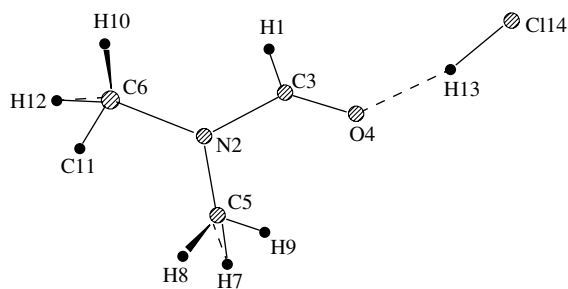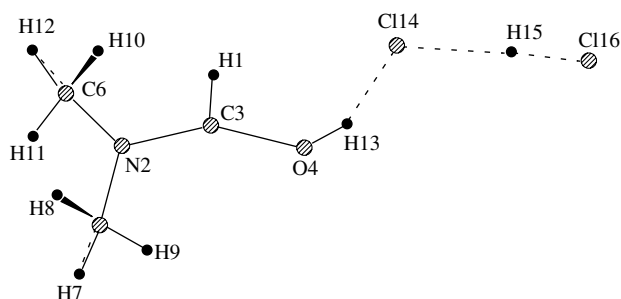
Fig. 1. Structure of the DMF · HCl complex.

Fig. 2. Structure of the DMF · (HCl)$_2$ complex.

For the study, we chose acid–base (1 : 1 and 1 : 2) complexes formed by the molecules of *N,N*-dimethyl-formamide (DMF) and HCl. The solutions of HCl in DMF were studied in detail by IR [6] and Raman spectroscopy [4] in the liquid phase and by the X-ray diffraction method in the solid phase [5]. It was found that quasi-ionic pairs and anions (AHA)⁻ are formed. These findings allow correct evaluation of the calculated results.

DISCUSSION

Calculated Data

To solve the problem formulated above by *ab initio* calculations using the GAMESS program package [12], we studied the molecules of HCl and DMF and the complexes (HCl)$_2$, DMF · HCl (Fig. 1), and DMF · (HCl)$_2$ (Fig. 2). All quantum chemical calculations were carried out using the self-consistent field methods in the basis set 6–31G, which is optimal for obtaining reliable data on the structures of such many-atom systems. Analysis of the stationary points obtained in the calculation of the potential energy surface for the systems under study showed that the Hessian eigenvalues (frequencies of normal vibrations) are positive in all cases. The values of the full energy and geometries of the studied acid–base complexes, which correspond to the found minimums on the potential energy surface, are described in Table 1. Data on Mulliken charges at the atoms are shown in Table 2.

The results of calculation show that, upon the addition of the HCl monomer ($E = -460.037173$ au) to the DMF molecule (that is, upon the formation of the 1 : 1 complex), the length of the intramolecular bond and charges at the atoms that form this bond are typical of a hydrogen bond with a moderate strength. The elongation of the covalent HCl bond from 1.295 to 1.338 Å also points to the fact that it formed a hydrogen bond, which is not strong.

Upon the addition of the dimer (HCl)$_2$ ($E = -920.076589$ au) to the DMF molecule, a proton transfers with the formation of a covalent OH bond with a length smaller than 1 Å. The remaining triatomic fragment Cl···HCl is almost linear and has a pronounced symmetry (Table 1) in contrast to the hydrogen chloride

dimer ($R_{ClH} = 1.296$ Å, $R_{Cl···H} = 2.799$ Å). Note that the triatomic fragment under consideration has a great negative overall charge (–0.851 au). Charges at the atoms with nos. 13–16 in Fig. 2 (Table 2) differ substantially from the corresponding charges at the atoms in the dimer (HCl)$_2$: 0.211, –0.203, 0.202, and –0.210 au.

Geometric parameters of the DMF molecule remain almost the same upon the formation of both complexes, although the distribution of charges at its atoms changes substantially. On average, the charges change by 7% in the 1 : 1 complex and by 22% in the 1 : 2 complex. The maximal changes (by 0.034 au (21%) and 0.161 au (100%)) are observed at the hydrogen atom of the formate group.

Comparison with the Condensed Phase

In contrast to calculated data for the isolated DMF–HCl complex with a 1 : 1 composition, the formation of A···H···B complexes with a strong quasi-symmetric hydrogen bond was found for the solutions and the solid phase [4–6]. For the crystalline complex, the lengths of O4-H13 and H13-Cl14 bonds (henceforth, numbers refer to the atoms in Figs. 1 and 2) are 1.097 and 1.723 Å, respectively [5]. That is, when one switches from the isolated complex to the condensed phase, the degree of proton transfer in the complex with a 1 : 1 composition substantially changes, which is an indication of the participation of the molecular environment in the step of proton transfer. This agrees with the results of studies of the acid–base complex structures in the gas phase. The interaction of the strongest proton donors and acceptors, such as trifluoroacetic acid, HCl, and aliphatic amines, stops when the molecular complex is formed [9, 10].

An increase in the positive charge at the hydrogen atom (no. 1) in the formate group (Table 2) in the formation of the 1 : 1 complex points to the possibility of the interaction of this hydrogen atom with the chlorine atom of another complex and the formation of the dimer DMF · (HCl)$_2$. This may stimulate the more complete transfer of proton 13. Indeed, the dimerization of quasi-ionic pairs of HCl with DMF was experimentally found in the crystalline phase [5].

Table 1. Full energy (E, au), equilibrium bond lengths (R, Å), and angles (α, deg) of the DMF molecule and complexes DMF · HCl and DMF · (HCl)$_2$

	Parameter*	DMF	DMF · HCl	DMF · (HCl)$_2$
E		−246.875037	−706.929444	−1166.983999
	C3-H1	1.082	1.080	1.074
	N2-C3	1.349	1.332	1.291
	C3-O4	1.225	1.237	1.288
	N2-C5	1.454	1.459	1.471
	N2-C6	1.450	1.455	1.469
	C5-H7	1.084	1.083	1.080
	C5-H8	1.084	1.083	1.081
R	C5-H9	1.077	1.076	1.075
	C6-H10	1.079	1.081	1.079
	C6-H11	1.084	1.083	1.080
	C6-H12	1.084	1.083	1.080
	O4-H13	–	1.656	0.996
	Cl14-H13	–	1.338	2.013
	Cl14-H15	–	–	2.214
	Cl16-H15	–	–	1.319
	N2-C3-H1	113.8	114.8	120.9
	H1-C3-O4	120.8	120.5	117.7
	N2-C3-O4	125.4	124.7	121.4
	C3-N2-C5	120.7	121.0	122.3
	C3-N2-C6	121.9	121.8	121.1
	C5-N2-C6	117.4	117.2	116.5
	N2-C5-H7	110.4	110.1	108.9
	N2-C5-H8	110.4	110.0	109.2
	N2-C5-H9	109.0	109.2	109.8
	N2-C6-H10	110.2	110.3	110.2
α	N2-C6-H11	110.7	110.3	109.5
	N2-C6-H12	110.7	110.4	109.4
	H7-C5-H8	108.6	108.9	109.5
	H7-C5-H9	109.2	109.3	109.8
	H8-C5-H9	109.2	109.4	109.7
	H10-C6-H11	108.4	108.5	109.2
	H10-C6-H12	108.3	108.5	109.1
	H11-C6-H12	108.4	108.7	109.4
	C3-O4-H13	–	129.4	112.3
	O4-H13-Cl14	–	176.1	146.9
	H13-Cl14-H15	–	–	132.8
	Cl14-H15-Cl16	–	–	177.1

* Atom numbering is the same as in Figs. 1 and 2.

Table 2. Charges at the atoms (au) in the DMF molecule and DMF · HCl and DMF · (HCl)$_2$ complexes

Atom*	DMF	DMF · HCl	DMF · (HCl)$_2$
H1	0.161	0.195	0.322
N2	−0.788	−0.779	−0.754
C3	0.572	0.620	0.646
O4	−0.604	−0.670	−0.696
C5	−0.220	−0.226	−0.242
C6	−0.205	−0.213	−0.232
H7	0.165	0.178	0.206
H8	0.165	0.177	0.208
H9	0.231	0.240	0.259
H10	0.173	0.181	0.214
H11	0.174	0.187	0.214
H12	0.174	0.187	0.213
H13	–	0.247	0.494
Cl14	–	−0.324	−0.792
H15	–	–	0.229
Cl16	–	–	−0.289

* Atom numbering is the same as in Figs. 1 and 2.

According to calculation, the interaction of the DMF molecule with the dimer (HCl)$_2$ results in proton transfer onto the base molecule. The same result was obtained experimentally for the solutions of HCl in DMF in excess acid [6]. The difference is that the (Cl···H···Cl)$^-$ anion formed by a strong symmetric hydrogen bond [6, 7] is the counter-ion in the liquid phase, whereas the asymmetric Cl...HCl fragment with the distances Cl14–H15 2.21 Å, H15–Cl16 1.32 Å, and the angle Cl14–H15–Cl16 177.1 Å is the counter-ion in the isolated complex. In the dimer (HCl)$_2$, these distances are 2.799 and 1.296 Å, and the angle is 167.4°. In the chlorine anions coordinated by hydrogen chloride in the solid phase [13], these distances are 1.649 and 1.471 Å; that is, anions have structures close to symmetric. The calculated asymmetry of the Cl14–H15–Cl16 fragment should decrease under the influence of the interaction of the terminal chlorine atom in the DMF complex · (HCl)$_2$ with atom H1 of the DMF molecule of a neighboring complex. This was in fact observed in the solutions.

Changes in the charges at the atoms of the DMF molecule under the action of the HCl monomer and the (HCl)$_2$ dimer with which it forms a hydrogen bond suggest that the involvement of DMF in the composition of complexes is accompanied by the substantial distribution of electron density (Table 2). This, in turn, allows us to expect that a number of force constants of bonds and angles in this molecule may also change noticeably. Indeed, a substantial difference in the IR spectra of DMF and HCl solutions in DMF are observed [6].

Thus, according to calculations, DMF forms a 1 : 1 molecular complex with HCl in the isolated state. In excess HCl, acid–base interaction radically changes and a proton transfers onto the DMF molecule to form the Cl...HCl fragment as in the liquid phase. To model acid–base interaction in the liquid phase and elucidate the role of molecular environment in proton transfer, it is promising to carry out further calculations of the isolated dimer (DMF · HCl)$_2$ and the heterocomplex (DMF · HCl) · (DMF · (HCl)$_2$.

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