



Solvent effect on proton transfer in the complexes of N,N-dimethylformamide with sulfuric and phosphoric acid: A DFT investigation

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ARTICLE INFO

Article history:

Received 27 June 2015

Received in revised form

2 October 2015

Accepted 9 November 2015

Available online 14 November 2015

Keywords:

Hydrogen bonds

Proton transfer

Phosphoric acid

Sulfuric acid

N,N-dimethylformamide

DFT calculations

ABSTRACT

Ab initio quantum-chemical calculations of structure and energies of the complexes of N,N-dimethylformamide (DMF) with sulfuric (H_2SO_4) and phosphoric (H_3PO_4) acids have been carried out. It has been found that the hydrogen bond between H_2SO_4 and DMF molecules is a little shorter and stronger than that between H_3PO_4 and DMF. The H-bond strength is different both in acid–acid and (acid)_n–DMF complexes for $n = 1, 2$. The polar solvent effect is taken into account by using the CPCM approach. The differences of geometric parameters of the H-bonds in the gas phase and DMF are analyzed. The potential energy surface (PES) of the proton transfer reaction in acid–DMF and (acid)₂–DMF complexes was calculated. The calculations have shown that the gas phase PES has a single distinct minimum (with the exception of the $(\text{H}_2\text{SO}_4)_2$ –DMF). In DMF, the proton transfer reaction takes place in all complexes, if $\text{O}_{\text{ACID}} \dots \text{O}_{\text{DMF}}$ distance is constrained. The solvent effect favors a proton transfer from sulfuric acid to oxygen atom of DMF molecule and formation of stable ionic pairs.

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1. Introduction

Understanding at the microscopic level, interpretation and prediction of mechanisms and kinetics of proton transfer reactions in polar solvents is a challenging objective of contemporary research in theoretical chemistry [1–3]. The theoretical investigations begin with searching for H-bonded complexes which can be important in proton transfer reactions. An elementary chemical process involves a computation of potential energy surface [4]. Since proton transfer occurs mostly in solution, it is important to consider environmental effects [5]. This can be performed in the form of either molecular dynamics (MD) simulation [6–11] or continuum solvent models [12–14].

The proton transfer is fundamental for the function of a fuel cell. It is well known that proton conducting gels can be obtained by doping of polymers with phosphoric acid [15,16]. Meanwhile, the application of superacids as H_2SO_4 leads to the stable gel-electrolytes with relatively high proton conductivity [17,18]. Nowadays, the level of the basic research into the structure of non-aqueous solutions of sulfuric acids is still insufficient whereas the

H_3PO_4 –DMF system has previously been investigated by different physico-chemical [19] and theoretical [20–24] methods. These studies provide the basis for concluding that strong intermolecular interactions result from hydrogen bonding in the system.

The mechanisms of proton transport in liquid phosphoric acid have already been proposed by Kreuer et al. [25,26]. Ab initio modeling of proton transfer in phosphoric acid clusters consisting of two to six phosphoric acid molecules was performed [27]. The energy barrier for proton transfer between phosphoric acid molecules was determined using the potential energy surface scan method under different constraint to neighboring oxygen atoms. Earlier [24], the process transfer of a proton in the H_3PO_4 –DMF and H_3PO_4 –DMFH⁺ complexes wherein distance between the two oxygen atoms for the hydrogen bond is relaxed was studied. The proton transfer from phosphoric acid to DMF oxygen atom in the H_3PO_4 –DMF mixture at mol fraction $x(\text{H}_3\text{PO}_4) = 0.2$ was investigated using a combined approach, based on classical molecular dynamics (MD) simulations with subsequent semiempirical (AM1) calculations [22]. The results showed that the proton transfer reaction effectively occurs in the system. Until now, only theoretical studies are available for hydrated sulfuric acid complexes of different composition [28–32].

In this study, we have investigated the hydrogen bonding and

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proton transfer energetic in the complexes of N,N-dimethylformamide with sulfuric and phosphoric acid. We have also considered the H-bond formation between the acid molecules themselves. We have performed high-level ab initio quantum-chemical calculations for the potential energy surface of (acid)_n-DMF complexes for n = 1, 2. The effect of the solvent on the geometry of the H-bond is taken into account by using the Conductor Polarized Continuum Model (CPCM). This paper combines the earlier reported quantum-chemical data of the complexes of N,N-dimethylformamide with sulfuric [33] and phosphoric [20] acid in the gas phase.

Section 2 will give an overview of our computational methods, followed by the results discussion in Section 3 and our conclusions in Section 4.

2. Computational methods

All ab initio calculations were performed with the GAUSSIAN 09 suite of programs [34]. We applied the Becke three-parameter hybrid functional combined with Lee–Yang–Parr correlation functional (B3LYP) which is the most frequently used density functional theory (DFT) and gives reasonable results for H-bonded complexes [35]. Using the same level of theory the binding strength (due to H-bonding) and proton transfer in the (H₃PO₄)_n clusters for n = 2–6 [27], and the solvation of DMF with hydrogen chloride, HCl [36–38] and hydrogen fluoride, HF [39] have been investigated. The 6–31++G(d,p) and cc-pVQZ basis sets were used.

We tested the accuracy of quantum-chemical calculations on single phosphoric and sulfuric acids and DMF molecules for which the experimental geometries are available (see Supporting Information, Table S1–S3). The 6–31++G** basis set was chosen because it provides a good agreement of geometry with gas-phase electron diffraction for DMF molecule [40] and X-ray diffraction data of phosphoric acid [41]. Unfortunately, calculation in such basis set was not suitable for sulfuric acid molecule. The differences for intramolecular distances of the H₂SO₄ between the data calculated from that basis set and the experimental values are relatively high, especially for the S=O and S–O bonds. The extension of the basis set from 6 to 31++G(d,p) (and similar basis sets [30,42]) to cc-pVQZ [33] shows the well known sensitivity of the S=O bond lengths with respect to computational efforts. This is why the second cc-pVQZ basis set was used. The geometrical parameters of the H₂SO₄ obtained with the B3LYP/cc-pVQZ basis set are shown to agree with the data determined from microwave spectra of gaseous H₂SO₄ molecules [43].

The earlier optimized geometries of the H-bonded complexes in the gas phase were taken as initial configurations for the B3LYP–CPCM computations. An effect of solvent is taken into account by using the CPCM approach [44]. In the CPCM model, the complex under investigation is placed in a cavity surrounded by a polarizable continuum (instead of explicit solvent molecules) with a dielectric constant ($\epsilon = 37.2$ for DMF), whose reaction field modifies the energy and the properties of the solute. The dielectric constant is $\epsilon = 1$ within the inner cavity. The cavity is described by contour of overlapping van-der-Waals spheres of each atom.

The minimum-energy states of the complexes were confirmed by calculating the harmonic frequencies.

The Basis Set Superposition Error (BSSE) was evaluated by the Counterpoise (CP) Correction [45]. The binding energy was calculated as follows:

$$\Delta E = E(AB, aUb, R) - [E(A, a, R) + E(B, b, R)] \quad (1)$$

and

$$\Delta E_{corr} = E(AB, aUb, R) - [E(A, aUb, R) + E(B, aUb, R)], \quad (2)$$

where $E(AB; aUb; R)$, $E(A; a; R)$, $E(B; b; R)$ are the energies of the AB complex and A and B monomers, respectively. R is the distance between A and B molecules in the AB complex; a and b is the basis set functions of A and B monomers and aUb is the basis set function of the AB complex. The BSSE-corrected binding energy is given as $\Delta E - \Delta E_{corr}$.

The geometric criterion of the H-bond has been used for H-bonding analysis [46]. The three types of the H-bonding criteria which are most frequently mentioned in the literature are weak, moderate and strong (see Table 1).

The energy barrier for proton transfer in (acid)_n-DMF complexes for n = 1, 2 was determined using the potential energy surface scan method as implemented in GAUSSIAN 09. It should be noted that for most proton transfer mechanisms there is a conflict between the high rates of proton transfer and the structural reorganization. Proton makes quick jumps back and forth between two heavy atoms on the hydrogen bond [46]. The actual proton transfer takes place in femtosecond (fs) timescale and the lifetimes are shorter than the local H-bond structure reorganization [47,48]. The results from the theoretical investigation [24] were shown that for the proton transfer both in the H₃PO₄-DMF and H₃PO₄-DMFH⁺ complexes the O_{ACID} ... O_{DMF} distance insignificantly changes (approximately 0.2 Å) in comparison with the O ... H distance for the proton involved in the hydrogen bond, namely it is more 1.0 Å. This is why we examined two cases, where, in the first case, the O_{ACID} ... O_{DMF} distance for the hydrogen bond considered is fixed, and no constraints are imposed in the second case. A hydrogen atom was transferred between the oxygen atoms of acid and DMF molecules in H-bonded complexes with an incremental distance of 0.05 Å. At each point of the scan, the transition structure was optimized with and without constraint on the equilibrium O_{ACID} ... O_{DMF} distance, and the energy value was assigned to the one obtained for the initial complex. The proton transfer coordinate is considered as:

$$\delta = r(O_{ACID} - H) - r(O_{DMF} - H) \quad (3)$$

where O_{ACID} and O_{DMF} are the two oxygen atoms between which the proton is moved.

3. Discussion

The optimized structures of the hydrogen bonded neutral complexes and ion pairs in DMF are shown in Fig. 1. It should be noted that the solvent effect significantly influences the structure of the complexes of sulfuric acid with DMF. Through optimization at the B3LYP–CPCM level we have obtained new structures in which proton is bonded to DMF oxygen atom, namely ion pairs of the [HSO₄][DMFH⁺] and [H₂SO₄HSO₄][DMFH⁺] (Fig. 1b–c). Meanwhile, the structure of the acid dimers, H₃PO₄-DMF and (H₃PO₄)₂-DMF remains almost unchanged in the gas phase as well as in DMF. The calculated values of the H-bonds geometric parameters in the complexes were investigated in the gas phase [20,33] and DMF and the corresponding energies are given in Tables 1 and 2. The B3LYP–CPCM level with both basis sets predicts very close structures of the complexes but different values of the geometric and energetic parameters.

First of all, let us compare the results obtained for acid dimers in DMF (see Fig. 1a). The most stable dimeric structure of both acids is a cyclic form with the molecules connected by two identical hydrogen bonds of moderate length (see Table 1). The H-bonds in the (H₃PO₄)₂ are significantly shorter than in the (H₂SO₄)₂. As

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