Hydration and protonation of *O*-vinylacetoxime in the gas phase: an *ab initio* study

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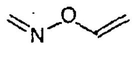
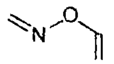
Ab initio HF/6-31G* calculations of *O*-vinylacetoxime monohydrates and cations were performed. Each conformer forms two stable H-complexes with participation of N and O atoms. The former have planar heavy-atom skeletons, whereas the water molecule in the latter is located above the plane of the proton-acceptor complex. The complexes stabilized by N...HO and O...HO bonds have different dipole moments and frequencies of the OH stretching vibrations. The most energetically favorable cation is formed by adding a proton to the $C_β$ atom of the vinyl group of *O*-vinylacetoxime. The *ap,ap*-conformer (*ap* is antiperiplanar) of this cation is 6.5 and 34.9 kcal mol^{-1} more stable than the onium cations with the NH^+ and OH^+ fragments, respectively, and is characterized by polarization and appreciable lengthening of the N—O and C=C bonds.

Key words: *O*-vinylacetoxime, H-complexes, cations, structure, *ab initio* quantum-chemical calculations, dipole moments, frequencies of stretching vibrations.

O-Vinyloximes obtained by direct *O*-vinylation of oximes by acetylene[1—4] or by addition of oximes to ethyl propyolate in the presence of catalytic amounts of triphenylphosphine[5] are interesting synthons and potential polydentate ligands. Recently, the structure of *O*-vinyloximes has been studied theoretically and experimentally. The problem of conformational isomerism of *O*-vinylacetoxime (**1**) was considered using the results of quantum-chemical calculations, IR and NMR studies, and measurements of the dipole moments.[6,7] According to *ab initio* calculations,[6] the molecules of **1** exist in the gas phase as an equilibrium mixture of two stable conformers **1a** (*ap,ap*) and **1b** (*ap,sp*) in an 82 : 18 ratio (here, *ap* and *sp* are antiperiplanar and synperiplanar, respectively).



1a (*ap,ap*)



1b (*ap,sp*)

The dipole moments of both conformers calculated in the 6-31G* basis set virtually coincide and are in good agreement with experimental values measured in octane.[7] However, measurements of the dipole moment of *O*-vinylacetoxime in solutions at different temperatures have shown[7] that, even in octane with a low dielectric constant ($ε$ = 1.95),[8] the solutions contained small amounts of conformers of molecule **1**, whose polarity was greater than that obtained from gas-phase calculations. The concentration of polar conformers increases as temperature increases as well as on going from octane to THF ($ε$ = 7.42)[8]. It was reasonable to assume that the structure of stable conformers of molecule **1** is closely related to their tendency to form complexes with hydrogen bonds (H-complexes). Intramolecular H-bonds in different conformations of the molecules of substituted oximes have been studied by X-ray structural analysis[9] and by the *ab initio* and PM3 quantum-chemical methods.[10]

In this work, we report the results of *ab initio* calculations in the 6-31G* basis set of *O*-vinylacetoxime monohydrates carried out taking into account conformational isomerism of molecule **1** and its ability for polydentate coordination. The structures of different types of H-complexes were determined, the complexation energies were calculated, and the charge distributions on the atoms and the frequencies of normal vibrations of water molecules in the associates were analyzed. Protonated forms of the molecules of compound **1** were also considered.

Results and Discussion

Structure and energetics. *Ab initio* calculations of H-complexes of the *O*-vinylacetoxime molecule carried out with full geometry optimization in the 6-31G* basis set using the GAUSSIAN-94 program package[11] were performed using the data obtained[7] for two stable planar conformers **1a** and **1b** as input parameters. The N and O atoms, as well as the $C_β$ atom of the vinyl group were considered as basic or nucleophilic sites of molecule **1**.

The calculated geometric parameters of initial conformers **1a,b** and hydrated forms (**2a,b** and **3a,b**) of

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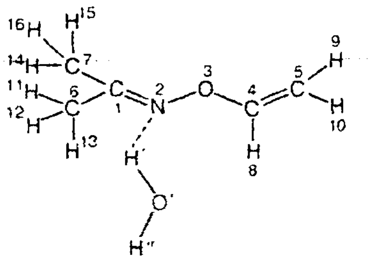
Table 1. Bond lengths (*d*) and bond angles (φ) in the molecules of *O*-vinylacetoxime and its hydrated and protonated forms

Parameter	**1a** (**1b**)	**2a** (**2b**)	**3a** (**3b**)	**4**
Bond		*d*/Å		
C(1)—N(2)	1.257	1.258	1.258	1.267
	(1.257)	(1.259)	(1.258)	
N(2)—O(3)	1.378	1.375	1.385	1.470
	(1.377)	(1.378)	(1.385)	
O(3)—C(4)	1.354	1.357	1.358	1.232
	(1.354)	(1.354)	(1.359)	
C(4)—C(5)	1.315	1.314	1.315	1.474
	(1.316)	(1.316)	(1.315)	
N(2)—H′	—	2.152	—	—
	—	(2.174)	—	
N(2)—O′	—	3.103	—	—
	—	(3.108)	—	
O(3)—H′	—	—	2.139	—
	—	—	(2.154)	
O(3)—O′	—	—	3.075	—
	—	—	(3.065)	
Angle		φ/deg		
N(2)—H′—O′	—	174.0	—	—
	—	(166.7)	—	
O(3)—H′—O′	—	—	168.3	—
	—	—	(160.4)	

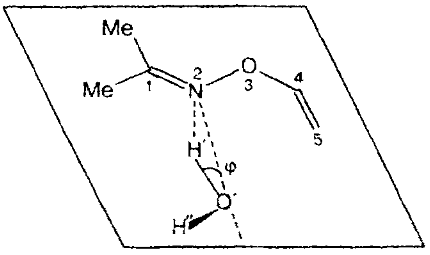
molecule **1** are listed in Table 1. The numbering of atoms for one of the H-complexes (Scheme 1) was also accepted for other (hydrated, protonated, and free) systems. No experimental data on the geometry of molecule **1** are available to date. Nevertheless, the good agreement between the calculated and measured values of the dipole moment of molecule **1**[7] confirms indirectly that the molecular structure is reproduced satisfactorily. Previously,[12] *ab initio* calculations (with the 6-31G* basis set) of hydrated and protonated forms of pyrrole and imidazole molecules have demonstrated a satisfactory agreement between the calculated and experimental geometries.

Scheme 1



According to our calculations, the O—H bond length (0.947 Å) and the H—O—H bond angle (105.5°) of the water molecule in its H-complexes with *O*-vinylacetoxime change only slightly. The O—H bond is lengthened by 0.003—0.005 Å, while the maximum variation of the bond angle is 0.4°. In the H-complexes, changes in the lengths of the bonds between the heavy atoms of molecule **1** and in the corresponding bond angles do not exceed 0.003 Å and 0.4°, respectively. The 1 : 1 H-complexes of oxime **1** are planar and correspond to initial *ap*,*ap*- or *ap*,*sp*-rotamers. In the H-complexes with the shortest *r*(O′—N) distance between the O′ atom of the water molecule and the N atom of oxime (**2a** (*ap*,*ap*) and **2b** (*ap*,*sp*)), the O′ atoms lie virtually in the plane of the C(1)=N(2)—O(3) fragment (Scheme 2). The θ(O′N(2)O(3)C(1)) torsion angle and the H′O′N(2) bond angle (φ) in monohydrate **2a** (**2b**) is 178.7° (170.4°) and 4.2° (9.3°), respectively.

Scheme 2

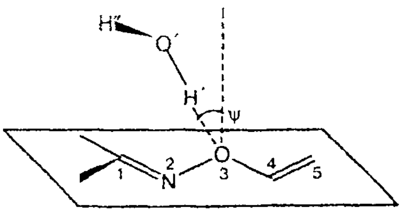


2b

The O′ atoms in H-complexes **3a** (*ap*,*ap*) and **3b** (*ap*,*sp*) with the shortest distance (*r*(O′—O)) between oxygen atoms of the water and *O*-vinylacetoxime molecules (the O′ and O(3) atoms, respectively) lie above the plane of the =N(2)—O(3)—C(1)= fragment (Scheme 3). The θ(O′O(3)N(2)C(1)) torsion angle in **3a** (**3b**) is 130.5° (110°), whereas the H′O′O(3) bond angle (φ) is 8.1° (13.6°). The ψ angle between the normal to the O(3)N(2)C(1) plane and the O′—O(3) axis in **3a** is ~45°, whereas in **3b** it is close to 35°. Such an orientation of the O′ atom of the water molecule is well suited for the formation of a multicenter hydrogen bond involving the H atom of the water molecule, the lone electron pair of the O(3) atom, and the π-electron system of the vinyl group. This is also supported by the fact that the H′—O(3)—C(4) bond angle is less than 135°.[13] However, the distance between the O′ atom and the C atom of the vinyl group in complexes **3a** and **3b** exceeds 4 Å, which indicates the formation of ordinary two-center hydrogen bonds. The *r*(O′—N) distances in associates **2a** and **2b** differ by 0.005 Å, whereas the *r*(O′—O) distance in **3a** is 0.01 Å longer than in **3b**. In all the H-complexes, the H″ atom of the water molecule is separated from the heavy atoms of molecule **1** by more than 4 Å.

Particular emphasis was placed on the H-complexes of the *ap*,*ap*- and *ap*,*sp*-conformers, in which the water molecule forms two hydrogen bonds, namely, a bond with the N(2) or O(3) atom and a bond with the C_β

Scheme 3



3a

atom of the vinyl group. According to calculations, these H-complexes are unstable compared to the equilibrium state with one H-bond.

The total energies (E_{tot}) of four stable H-complexes (**2a,b** and **3a,b**) and their formation energies (ΔE) are listed in Table 2. The ΔE values were calculated as the differences between the E_{tot} values and the sum of the total energies of the water molecule and the corresponding conformer of molecule **1** and then corrected for zero-point vibrational energies (*ZPE*) of the free molecule and its hydrated forms. In addition, the basis set superposition error (*BSSE*) was calculated for the association energy by the equalization method.[14]

The formation energies of *O*-vinylacetoxime monohydrates calculated with inclusion of *ZPE* correction vary from −2.8 to −3.5 kcal mol^{-1}. According to calculations carried out in the same basis set,[12] the energy gain obtained in the case of coordination of a water molecule to the N(3) atom of the imidazole molecule is much greater (−7.1 kcal mol^{-1}), whereas that obtained in the case of a π-complex of the pyrrole molecule with water is nearly the same (−3.7 kcal mol^{-1}). The maximum range of changes in the formation energy (ΔE) for H-complexes **2a,b** and **3a,b** is ~2 kcal mol^{-1}, whereas the differences between the ΔE values in this series do not exceed 0.7 kcal mol^{-1} (see Table 2). At the same time, the range of changes in the ΔE values obtained from calculations with inclusion of *BSSE* varies for these H-complexes from 1.3 to 1.9 kcal mol^{-1}. These data show that the estimates of stability of the monohydrates considered and, hence, of their statistical distribution in the equilibrium mixtures are inadequate. The use of an extended basis set also does not improve the situation, since the range of the heats of formation[15,16] does not change appreciably in this case.

Table 2. Total energies (E_{tot}/au), formation energies (ΔE/kcal mol^{-1}), zero-point vibrational energies (*ZPE*/kcal mol^{-1}), and dipole moments (μ/D) of initial conformers, H-complexes, and protonated forms of molecule **1** calculated in the 6-31G* basis set

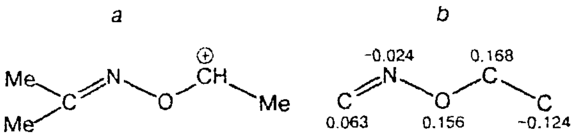
Compound	$-E_{tot}$[a]	$-\Delta E$	*ZPE*	$-\Delta E$ range[b]	μ
1a	323.8024				2.01
1b	323.8014				2.07
2a	399.8213	5.1	3.4	1.5—3.4	3.43
2b	399.8205	5.3	3.5	1.9—3.5	2.97
3a	399.8202	4.4	2.9	1.6—2.9	2.22
3b	399.8189	4.3	2.8	1.4—2.8	2.00
4	324.1695	230.3	223.7		
5	324.1610	225.0	217.2		
6	324.1138	195.4	188.8		

[a] For H_2O, $-E_{tot}$ = 76.01 au.

[b] The energy range with inclusion of *BSSE*.

Unlike H-complexes, the magnitudes of the energy differences between the *O*-vinylacetoxime cations are large enough to be compared (see Table 2). Among these cations, cation **4** (Scheme 4, *a*), formed by adding a proton to the C_β atom of the vinyl group, has the highest energy.

Scheme 4



4

The onium cations with the NH^+ (**5**) and OH^+ (**6**) fragments are 6.5 and 34.9 kcal mol^{-1} less stable, respectively. The energy difference between these cations (28.4 kcal mol^{-1}) is much larger than that between the onium cations of oxime $H_2C{=}NOH$ (18.9 kcal mol^{-1}).[17] Cation **4** retains a planar *ap,ap*-skeleton; however, the N(2)—O(3) and C(4)—C(5) bonds become appreciably lengthened (see Table 1) and polarized (see Scheme 4, *b*, in which the changes in the atomic charges on protonation, Δq, are given in au).

Vibrational frequencies. Calculations of vibrational frequencies of stable conformers of *O*-vinylacetoxime and its hydrated forms were carried out in order to obtain the *ZPE* values (see Table 2) and to analyze the frequencies of the ν(OH) stretching vibrations of the water molecule in the H-complexes with different electron-donor centers of the oxime molecule (Table 3). The calculations were performed using a scale factor of 0.89, as has been recommended[11] for the 6-31G* basis set.

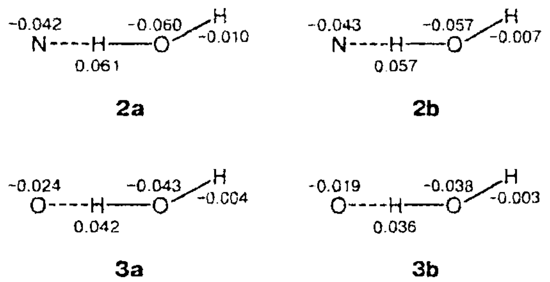
Table 3. Calculated* normal frequencies of stretching vibrations (ν) of the b_2 and a_1 types for the water molecule and H-complexes of *O*-vinylacetoxime

Molecule	ν**(OH)/cm^{-1}	
	b_2	a_1
H_2O	3729 (1.38)	3623 (0.43)
2a	3702 (3.81)	3591 (5.03)
2b	3700 (3.54)	3583 (4.24)
3a	3713 (3.15)	3613 (1.88)
3b	3712 (2.75)	3613 (1.94)

* Calculated using a scale factor of 0.89.

** The relative intensities of corresponding bands are given in parentheses.

Scheme 5



A greater decrease in the ν(OH) frequency of both asymmetric and symmetric vibrations in the H-complexes **2a,b** indicates that the H-bonds with the N atom are stronger than those with the O atom. Differences in the magnitudes of the shifts of the frequencies of asymmetric and symmetric ν(OH) vibrations for associates **2a,b** and **3a,b** are due to different spatial orientation of the water molecule with respect to the *O*-vinylacetoxime molecule. In the monohydrates in which the O atom of the water molecule lies in the plane of the heavy-atom skeleton of oxime **1**, the shift of the $\Delta\nu_{as}$ frequency is smaller than that of the ν_s frequency, namely, $\Delta\nu_{as} = 27$ cm^{-1} ($\Delta\nu_s$ = 38 cm^{-1}) for **2a** and $\Delta\nu_{as} = 29$ cm^{-1} ($\Delta\nu_s$ = 46 cm^{-1}) for **2b**. The opposite effect (larger shift of the ν_{as} frequency) occurs in nonplanar H-complexes **3a** ($\Delta\nu_{as}$ = 16 cm^{-1}, $\Delta\nu_s$ = 10 cm^{-1}) and **3b** ($\Delta\nu_{as}$ = 17 cm^{-1}, $\Delta\nu_s$ = 10 cm^{-1}). Therefore, by comparing the theoretical and experimental shifts of the frequencies of the O—H stretching vibrations of the water molecule in the H-complexes it is possible not only to reveal the coordination sites and to assess the relative strength of the H-bonds thus formed, but also to determine the spatial arrangement of the heavy atoms participating in these bonds.

Charge distributions and dipole moments. It is known that the dipole moments (μ) of stable conformers of *O*-vinylacetoxime (**1a,b**) are close.[6] The μ values of a particular type of *O*-vinylacetoxime monohydrates (**2a,b** or **3a,b**) also differ only slightly (by 0.46 and 0.22 D, respectively, depending on the coordination site) (see Table 2). Therefore, it is impossible to establish the conformation of a particular H-complex of oxime **1** using the experimental value of its dipole moment. However, since the dipole moments of molecule **1** and associates **3a,b** hydrated at the O atom are close, whereas those of the H-complexes **2a,b** are 1.0—1.2 D larger, one can attempt to determine the center of formation of the strongest H-bond by dielectrometric titration.

The formation of H-complexes is accompanied by electron density redistribution which involves both heavy atoms and peripheral H atoms. In all associates (**2a,b** and **3a,b**), the atoms participating in the formation of the H-bond are involved in the electron density redistribution to the greatest extent, the O—H...N or O—H...O fragments being particularly strongly polarized. As a result of complexation, the electron density on the bridging H atom decreases, whereas that on the heavy atoms increases (see Scheme 5 in which the Δq values are given in au).

The degree of charge transfer upon the formation of the H-complexes **2a**, **2b**, **3a**, and **3b** is very small (0.010, 0.007, 0.006, and 0.005 au, respectively).

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