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Protonation of *N*-alkenylacrylamides

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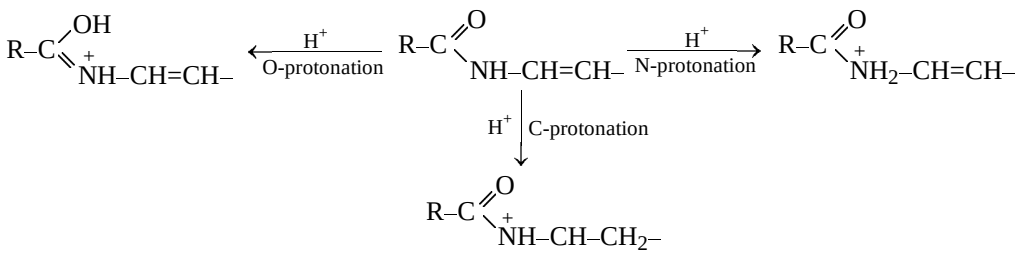
Abstract — Protonation of *N*-alkenylacrylamides and medium effects on the protonation direction were studied theoretically (DFT calculations) and experimentally (IR spectroscopy). In crystal, *N*-alkenylacrylamide hydrochlorides exist in the O-protonated form in contrast to acrylamide hydrochloride which exists in the N-protonated form.

Earlier it was shown that radical copolymerization of unsaturated amides with vinyl chloride is followed by polymer-like dehydrochlorination reactions of the polymer chains [1]. The evolved hydrogen chloride protonated amide fragments in the chains of the copolymers. It was established by IR spectroscopy that the copolymers with acrylamide form N-protonated salts, whereas the copolymers with its *N*-alkenyl-substituted derivatives, like *N*-(cyclohexen-1-yl)acrylamide, form O-protonated salts. Thus the IR spectra of acrylamide copolymers contain a broad absorption band at 3200–3400 cm^{-1}, that corresponds to N–H stretching vibrations in the NH_3^+ group. Besides, the absorption band at 1670 cm^{-1} is preserved in the spectrum, that is characteristic of stretching vibrations of a free carbonyl group and implies formation of N-protonated salts. On the contrary, in the IR spectra of *N*-(cyclohexen-1-yl)acrylamide copolymers, the band of C=O stretching vibrations is shifted to 1545 cm^{-1} and the absorption band of N–H stretching vibrations is observed at 3180–3290 cm^{-1}. These observations provide unequivocal evidence for the protonation on the oxygen atom.

The observed dualism in the behavior of acrylamide and its *N*-vinyl derivatives prompted us to investigate a general question of the direction of protonation of these compounds under various conditions.

Amides of saturated carboxylic acids were found to be protonated on the oxygen rather than nitrogen atom (see [2] and references therein). As to the direction of protonation of unsaturated amides, in particular, acrylamide, there is no unambiguous answer. According to high-level nonempirical calculations, the proton affinity of the oxygen atom in acrylamide is higher than that of the nitrogen atom [3]. At the same time, Perrin *et al.* [4, 5] obtained experimental evidence to show that the acid-catalyzed proton exchange in acrylamide occurs either by the N-protonation mechanism or, with amides containing electron-acceptor substituents at the carbonyl group, by the O-protonation mechanism via formation of imidic acid RC(OH)=NR'. Unsaturated groups on the nitrogen atom make possible, in addition to the O- and N-protonation mechanisms, a C-protonation mechanism involving formation of an immonium cation.

The aim of the present work was to determine the direction of protonation of *N*-alkenylacrylamides by studying their hydrochlorides by IR spectroscopy, as well as to perform a comparative theoretical analysis of the O-, N-, and C-protonated forms of *N*-vinylacrylamide using the density functional theory (DFT) method. The effect of specific (in the supermolecule approximation) and nonspecific (in the approximation of the IPCM continual model) solvation on the relative



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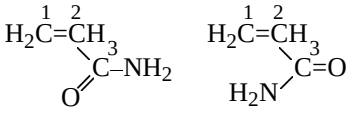
probability of protonation of various basicity sites in the molecule was also studied.

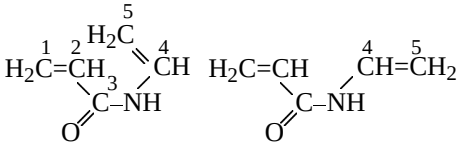
The IR study of hydrochlorides of monomeric acrylamide and its *N*-alkenyl derivatives gave the same results as those described above for their copolymers with vinyl chloride, that is, the formation of an N-protonated salt in the former case and O-protonated salts in the latter [5].

MP2(Full)/6-31G*//MP2(Full)/6-31G* calculations showed that the *s-cis* conformer of acrylamide (**I**) is 1.5 kcal mol^{-1} lower in energy than the *s-trans* conformer [3]. Our B3LYP/6-311G** calculations give virtually the same value (1.6 kcal mol^{-1}).

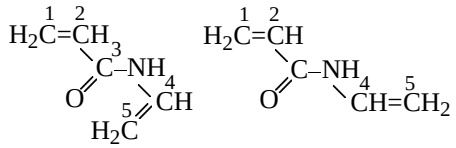


s-cis-**I** *s-trans*-**I**

Based on these results, we confined the analysis of the number of possible conformers of *N*-vinylacrylamide (**II**) by four structures (**IIa**–**IId**).



IIa **IIb**



IIc **IId**

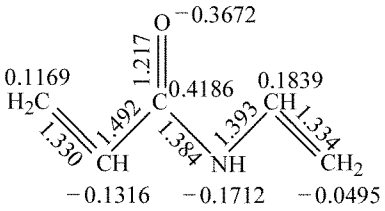
The four structures all correspond to local minima on the potential energy surface, their energy with respect to conformer **IIa** decreasing in the order (kcal mol^{-1}): **IIa** (0), **IIb** (–3.0), **IIc** (–3.6), and **IId** (–6.0). Taking this into account, all calculations for the protonated forms were performed for *s-cis*-**I** and **IId**.

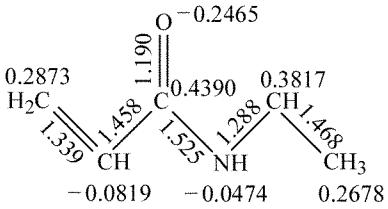
The calculated proton affinities (*PA*) for *s-cis*-**I** are 216.7 and 203.9 kcal mol^{-1} for O- and N-protonation, respectively. Detailed analysis of different protonated forms of acrylamide is given in [6]. In the present work we dwelt on the effect of solvation as a possible reason of the discrepancy between the results of calculations for an isolated molecule, which gave preference to O-protonation [3] and the experimental data which were indicative of N-protonation [5]. We made use of two approaches, viz. the Onsager solvation model as a model of nonspecific solvation and the supermolecule approximation as a model of specific solvation. The Onsager radii of the O- and N-protonated forms of *s-cis*-**I** are quite similar (3.68 and 3.63 Å, respectively), and the difference in the PA values decreases from 12.8 kcal mol^{-1} in the gas phase to 9.4 kcal mol^{-1} in a highly polar medium (ε 80), though the O-protonated form is still preferable. Specific solvation of the N- and O-protonated forms of acrylamide was simulated by their hydration with five water molecules in order to "solvate" the four atoms of the amide group as the most polar group in the molecule, and the positively charged center formed by protonation. The N-protonated form is hydrated on the three NH protons and on the carbonyl oxygen. The fifth water molecule does not coordinate to the carbonyl carbon, but, instead, geometry optimization predicts formation of a trimer of water molecules (Fig. 1). The hydration energy is 96.5 kcal mol^{-1}. The O-protonated form is hydrated by three water molecules on the OH and NH protons, while the other two water molecules coordinate neither with the carbonyl carbon nor with the nitrogen atom but form hydrogen bonds with other water molecules (Fig. 1). The hydration energy of the O-protonated form is 92.2 kcal mol^{-1}, that is, the energy difference between hydrated O- and N-protonated forms decreases by 4.3 kcal mol^{-1} as compared to the isolated forms in the gas phase.

Thus, the account for the effect of the medium in terms of both nonspecific and specific solvation results in a slightly increased relative probability of N-protonation of acrylamide as compared to the isolated molecule.

With *N*-vinylacrylamide (**IId**), protonation of the three basicity sites, namely, O, N, and C^5 atom, was studied. The maximum *PA* value is observed for protonation on the C^5 atom, 220.5 kcal mol^{-1}. A lower *PA* value was obtained for O-protonation (216.7 kcal mol^{-1}), and the lowest for N-protonation (200.2 kcal mol^{-1}). Comparing these results with those for acrylamide, one can see that the relative probability of O-protonation for N-vinyl acrylamide is much higher, namely, the PA difference increases from 12.8 kcal mol^{-1} for acrylamide to 16.5 kcal mol^{-1} for *N*-vinylacrylamide. These results are probably explained by the fact that the basicity of the nitrogen atom in the latter molecule is decreased by conjugation with the *N*-vinyl group, which simultaneously increases the basicity of the C^5 atom.

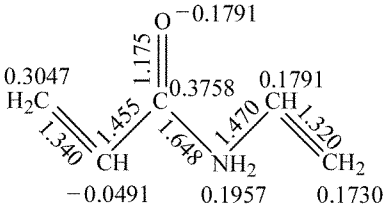
Let us consider changes in the geometry and electron distribution attendant in the O-, N-, and C-protonation of compound **IId** in the gas phase (the





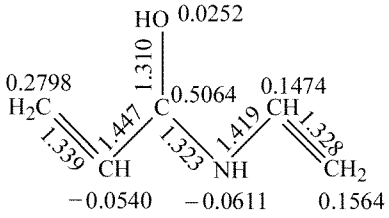
III(C^+)

PA 220.5 kcal mol^{-1}



III(N^+)

PA 200.2 kcal mol^{-1}

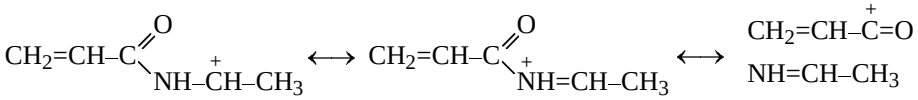


III(O^+)

PA 216.7 kcal mol^{-1}

charges on heavy atoms are summarized with the charges on hydrogen atoms attached to them).

The protonation direction does not notably affect the C^1–C^2 double bond but strongly changes the structure of the rest part of the molecule. C-Protonation leads to elongation of the C^4–C^5 bond, changing its order. At the same time, the substantial shortening of the N–C^4 bond and even more pronounced elongation of the C^3–N bond reflects strong conjugation of the nitrogen lone pair with the cationic center on the C^4 atom with simultaneous weakening of its conjugation with the carbonyl group, which can be represented as a contribution of the following resonance structures.



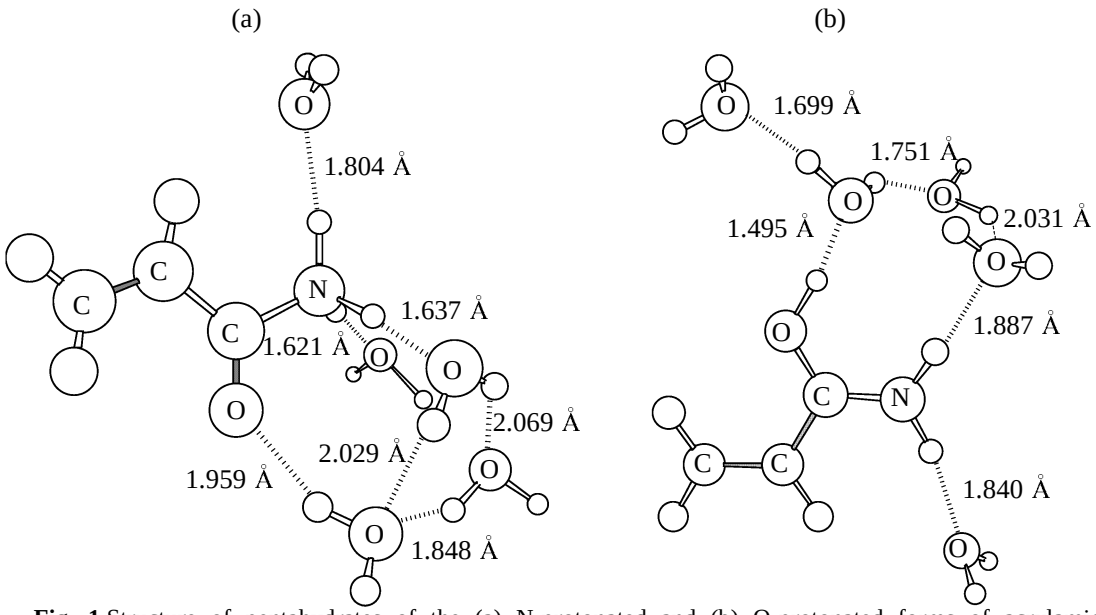
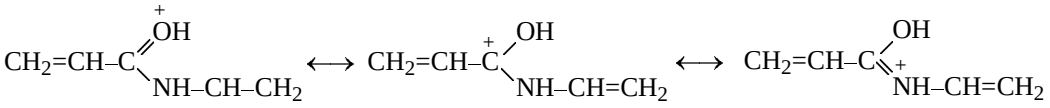
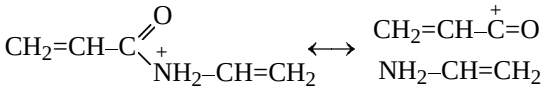


Fig. 1. Structure of pentahydrates of the (a) N-protonated and (b) O-protonated forms of acrylamide.

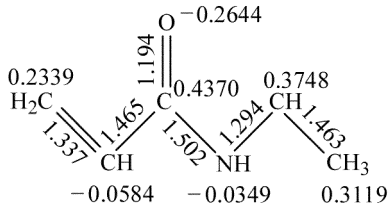
O-Protonation exerts the opposite effect on the structure of the amide fragment, and the O-protonated form can be represented as a superposition of the following structures.



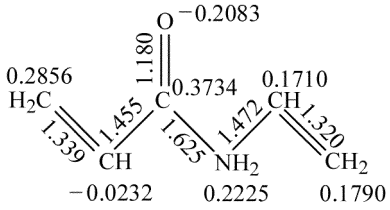
No p–π conjugation is possible in the N-protonated form, though the abnormally high length of the C^3–N bond is indicative of a notable contribution of the resonance structure without this bond and implies its loosening upon N-protonation.



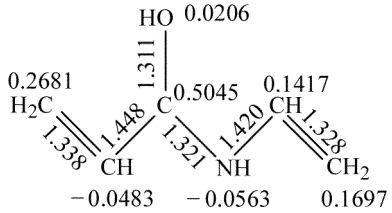
The Onsager radii of the C-, N-, and O-protonated forms of N-vinylacrylamide (**III**) differ only slightly, the effect of nonspecific solvation in a polar medium (ε 80) being ~3 kcal mol^{-1} for C- and N-protonation and practically absent for O-protonation.



r 4.00 Å, PA 223.7 kcal mol^{-1}



r 3.84 Å, PA 202.8 kcal mol^{-1}



r 4.14 Å, PA 216.9 kcal mol^{-1}

Therefore, as with acrylamide, the effect of nonspecific solvation decreases the relative probability of O-protonation by ~3 kcal mol^{-1} as compared to N-protonation.

Specific solvation of the C-, N-, and O-protonated forms of N-vinylacrylamide (**III**), simulated similarly as for the N- and O-protonated acrylamide in the supermolecule approximation by the calculation of pentahydrates of the corresponding forms, exerts a much more pronounced effect on the relative basicity of the different centers. The optimized hydrated C-protonated form has a structure corresponding to "solvation" of the carbonyl oxygen and NH proton by dimers of water molecules and interaction of the fifth water molecule of water with the α-carbon atom of the *N*-vinyl group. The N-protonated form is hydrated by one water molecule on one of the NH protons, whereas the other four water molecules form a linear tetramer that solvates by one its end the second NH proton and by the other end, the carbonyl oxygen (Fig. 2). The O-protonated form is hydrated on the OH proton by a trimer of water molecules and on the NH proton, by a dimer of water molecules. Therewith, inversion of the relative stability of the C- and O-protonated forms occurs: The most basic center in the isolated molecule both in the gas phase and in a polar medium is the α-carbon atom of the *N*-vinyl group, whereas the most basic center in the hydrated form is the oxygen atom. The hydration energy increases from the C-protonated form to the O- and N-protonated forms, equaling –76.4, –82.6, and –85.7 kcal mol^{-1}, respectively.

The above analysis allows the following conclusions. In the gas phase, both acrylamide and *N*-vinylacrylamide are protonated on the oxygen atom, the preference for O-protonation for *N*-vinylacrylamide being substantially stronger. Taking into account that the effect of the medium decreases in part the energy gap between O- and N-protonations, that is, the calculations reproduce the trend, while not reproducing the experimentally observed N-protonation for acrylamide. The experimental data were obtained by IR spectroscopy for hydrochlorides of acrylamide and its *N*-alkenyl derivatives in the crystal state where the

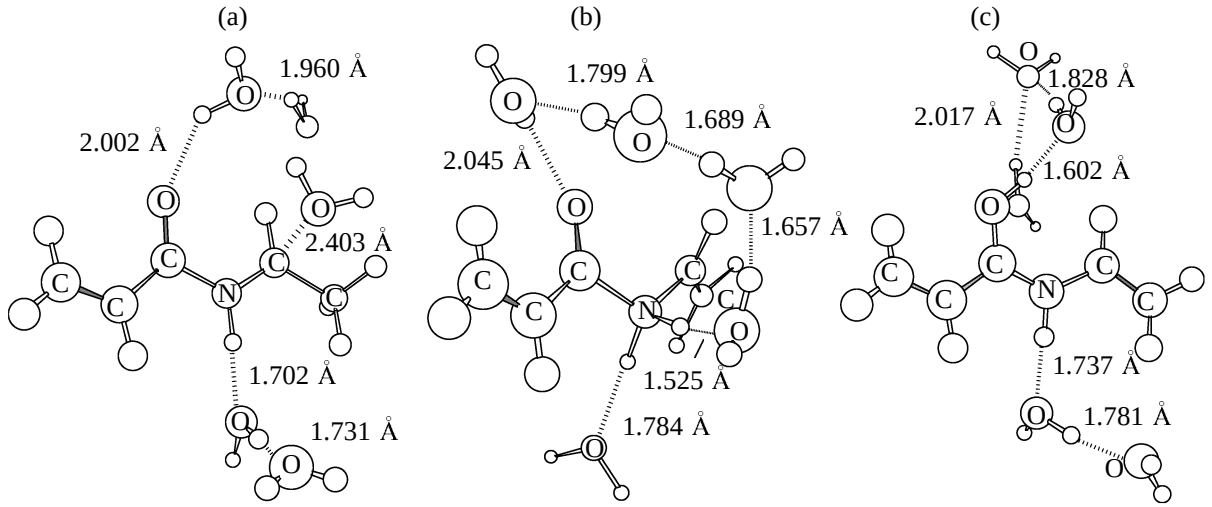
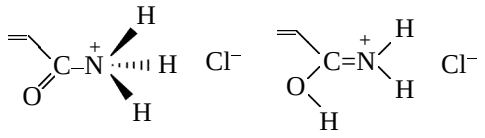


Fig. 2. Structures of pentahydrates of the a(a) C-protonated, (b) N-protonated, and (c) O-protonated forms of *N*-vinylacrylamide.

interaction between counter ions, that is not accounted for in the calculations, may play a significant role. Such interaction in N-protonated acrylamide (the sum of the charges on the three NH protons is 0.94 *e*) is substantially stronger than in the O-protonated form (the sum of the charges on the two NH protons is 0.58 *e*), and, probably, these ionic interactions are responsible for the fact that acrylamide hydrochloride in the crystal state exists as an N-protonated salt.



With *N*-alkenylacrylamides, this effect must be much weaker, firstly, because of the smaller number of NH protons and, secondly, because of the possible steric hindrances crated by the *N*-alkenyl group. For this reason, *N*-alkenylacrylamide hydrochlorides exist as O-protonated salts even in crystal.

The IR spectra were on a Specord IR-75 instrument in KBr pellets and mineral oil.

Geometry optimization for neutral and protonated forms was performed with the B3LYP hybrid potential with the 6-311G** basis set. All calculations were performed using the GAUSSIAN 98 program package [6].

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