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LETTERS TO THE EDITOR

"Vertical" and "Adiabatic" Proton Affinity

S. G. Semenov and M. V. Makarova

St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia
e-mail: mcmury@yandex.ru

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The protonation of some Brønsted bases is accompanied by a significant structural reorganization leading to a decrease in the rate of the processes of addition and detachment of the mobile protons. Such cases are considered as a combination of high thermodynamic basicity with low nucleophilicity [1] or with low kinetic basicity [2]. However, by analogy with the "vertical" ionization potential, which characterizes the process of the instantaneous removal of an electron, and the "adiabatic" ionization potential, which takes into account the difference between the equilibrium structural parameters of the cation and the parent molecule, it is possible to distinguish the "vertical" and "adiabatic" proton affinity (VPA and APA). In this report the quantum chemical method PBE0 using the cc-pVTZ orbitals for the nitrogen and mobile hydrogen and the cc-pVDZ orbitals for the carbon and for hydrogen atoms strongly bound to carbon and Gaussian-03 software [3] were applied to calculate the VPA and APA values for the quinuclidine and 1,8-bis(dimethylamino)naphthalene molecules.

The APA value is defined as the energy difference between the equilibrium structures of the base and the conjugate acid with or without accounting for the zero-point energy. The VPA magnitude is identified as the energy difference between the equilibrium structure of the base and the energy of the non-equilibrium structure of the conjugate acid, in which the structural parameters of the base remain the same, but the labile proton position corresponds to the constrained energy minimum.

In the case of $HC(CH_2CH_2)_3N \rightarrow HC(CH_2CH_2)_3NH^+$ the calculated difference between the APA (244.6 kcal mol^{-1}) and VPA (241.1 kcal mol^{-1}) is not large (3.5 kcal mol^{-1}). However, for 1,8-bis(dimethylamino)naphthalene (a proton sponge) the APA value (255.1 kcal mol^{-1}) is more than the VPA value (235.1 kcal mol^{-1}) by 20.0 kcal mol^{-1}. Taking into account the zero-point values, we obtain APA 246.9 kcal mol^{-1} (the experimental value is 246.2 kcal mol^{-1} [4]) and VPA = 246.9 – 20.0 = 226.9 kcal mol^{-1} (less than in the case of quinuclidine).

The VPA value may also be determined by another method. We calculated the equilibrium structural parameters and energy of the base while attaching the protons with the hydrogen orbitals centered on them to the unshared electron pairs and replacing the true charges of the protons with zero. Then, the charge of one proton was restored, but all structural parameters were left the same, and the acid energy was calculated. The difference of these energies for quinuclidine (240.1 kcal mol^{-1}) is by 1.0 kcal mol^{-1} less than the above VPA value. The N–H bond (0.999 Å) is shorter than the value of 1.017 Å corresponding to a constrained minimum by 0.018 Å. For the equilibrium configuration of the cation the same value of the N–H bond length but lower symmetry (C_3 instead of C_{3v}) were obtained. Due to the basis expansion at expense of the "floating" orbitals, we obtain the APA value reduced by 0.8 kcal mol^{-1}, and the difference between the APA (243.8 kcal mol^{-1}) and VPA (240.1 kcal mol^{-1}) values, equals to 3.7 kcal mol^{-1}, which is virtually identical to the difference between these values obtained by the first method.

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