



Revisiting the solvation enthalpies and free energies of the proton and electron in various solvents



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ABSTRACT

In scientific literature there are only several values for solvation enthalpies and free energies of the proton and electron, the quantities from which the enthalpies and free energies of the solvated proton and electron can be issued. The latter quantities are of significance in thermodynamic modeling of antioxidative properties in the media where the reactions really occur. This work fills this gap in scientific literature. Namely, a systematic investigation of the solvation enthalpies and free energies of the proton and electron in twenty commonly used solvents of different polarities was performed. For this purpose eleven *ab initio* and DFT methods were used in combination with the 6-311++G(d,p) basis set and SMD solvation model. Due to very good overall performance, B3LYP was selected for further computations with larger basis sets. The thermodynamic values obtained at the B3LYP/Aug-cc-pVTZ level of theory are in very good agreement with the existing several values for solvation enthalpies of the proton and electron, and they are recommended for application in the examinations of antioxidative activity in different solvents.

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1. Introduction

Antioxidative activity of various classes of compounds has been the subject of numerous experimental and theoretical studies. Theoretical investigations are often focused on the elucidation of the mechanisms through which compounds exhibit their ability to trap reactive free radicals by yielding more stable and less harming radical species. There are three major antioxidative mechanisms: HAT (Hydrogen Atom Transfer), SET-PT (Single Electron Transfer–Proton Transfer) and SPLET (Sequential Proton-Loss Electron-Transfer). These processes are usually described by the following thermodynamic quantities: BDE (Bond Dissociation Enthalpy), IP and PDE (Ionisation Potential and Proton Dissociation Enthalpy), and PA and ETE (Proton Affinity and Electron Transfer Enthalpy). For an antioxidative compound ArOH these enthalpies are defined as follows:

$$\text{BDE} = H(\text{ArO}^\bullet) + H(\text{H}^\bullet) - H(\text{ArOH}) \quad (1)$$

$$\text{IP} = H(\text{ArOH}^{+\bullet}) + H(\text{e}^-) - H(\text{ArOH}) \quad (2)$$

$$\text{PDE} = H(\text{ArO}^\bullet) + H(\text{H}^+) - H(\text{ArOH}^{+\bullet}) \quad (3)$$

$$\text{PA} = H(\text{ArO}^-) + H(\text{H}^+) - H(\text{ArOH}) \quad (4)$$

$$\text{ETE} = H(\text{ArO}^\bullet) + H(\text{e}^-) - H(\text{ArO}^-) \quad (5)$$

In Eqs. (1)–(5) H denotes the enthalpy of the parent molecule (ArOH), its radical cation (ArOH⁺), radical (ArO[•]), and anion (ArO[−]). Certainly, the analogous equations can be written where the enthalpies are replaced with free energies (G). The enthalpies (free energies) of the hydrogen atom (H[•]), proton (H⁺), and electron (e[−]) also figure in these equations, where the enthalpies (free energies) of the proton and electron cannot be calculated. The thermodynamic quantities for the gas-phase can be easily attained by inserting the commonly accepted values of 6.197 kJ mol^{−1} for the proton enthalpy (5/2RT, the value for an ideal gas), 3.146 kJ mol^{−1} for the electron enthalpy, −26.255 kJ mol^{−1} for the proton free energy, and −3.633 kJ mol^{−1} for the electron free energy [1]. The gas-phase values for $H(\text{H}^+)$, $H(\text{e}^-)$, $G(\text{H}^+)$, and $G(\text{e}^-)$ have been recently revised [2,3]. Under an assumption that the proton does not behave as a classical particle at all temperatures (lower than 120 K), the values of 6.1398 and −26.3424 kJ mol^{−1} for $H(\text{H}^+)$ and $G(\text{H}^+)$ were obtained by using a procedure based on the Fermi–Dirac formalism at the standard pressure of 1 bar [2]. A procedure which determines the entropy of the electron in the gas-phase was used to calculate other thermodynamic quantities of the electron, and the values of 3.1351 and −3.6160 kJ mol^{−1} were obtained for $H(\text{e}^-)$ and $G(\text{e}^-)$ [3].

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