Electron Transfer of Functionalized Quinones in Acetonitrile

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ABSTRACT

Quinones are a family of organic molecules that can undergo reversible redox reactions. They have been proposed to replace redox active metal species in energy storage devices. To estimate the output power of these devices, the kinetics of the underlying redox reactions must be understood. Marcus theory is a widely-accepted model of electron transfer in solution that can serve as a good starting point for studying the kinetics of redox reactions[1]. Assuming that solvent reacts linearly to the change in charge state of the reactant, Marcus established a relationship between the activation free energy and the solvent reorganization free energy.

One of the main advantages of organic molecules is the versatility of their molecular structure, which allows fine tuning of their chemical properties. According to Marcus theory, the reorganization free energy is only related to the radius of the reactant for the reactions in the same solvent if we assume a spherical reactant. However, this relation fails for most of molecular reactants that are not spherical. In a recent paper[2], we introduced a framework for computing the reorganization free energy using molecular density functional theory (MDFT). MDFT is a molecular liquid state theory developed to study solvation effects with numerical efficiency superior to expensive molecular simulations.

Here, we apply MDFT to calculate the reorganization free energy of electron transfer half-reduction reactions of functionalized Quinones solvated in acetonitrile. The influence of the position, number and volume of functional groups on the reorganization free energy is discussed. Inverse correlations between the number and volume of functional groups are found, while the position of the groups shows little effect.

REFERENCES

[1] Marcus, R.A. "Electron Transfer Reactions in Chemistry: Theory and Experiment (Nobel Lecture)", Angewandte Chemie International Edition in English, **32 (8)**, 1111-1121 (1993).
[2] Jeanmairet, G.; Rotenberg, B.; Levesque, M.; Borgis, D.; Salanne, M. "A molecular density functional theory approach to electron transfer reactions", Chem. Sci., **10 (7)**, 2130–2143 (2019).