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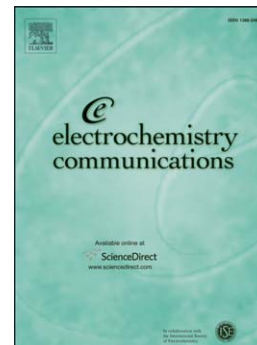
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The Redox Potential of the Phenyl Radical/Anion Couple and the Effect Thereon of the Lithium Cation: A Computational Study

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Abstract: The most popular $E_{\text{Ph}^{\bullet}/\text{Ph}^-}^0$ value is incorrect and cannot actually be obtained from the up-to-date experimental electrochemical data only. Quantum chemical calculations presented in this work showed that the accurate $E_{\text{Ph}^{\bullet}/\text{Ph}^-}^0$ values are equal to -1.28 , -1.27 and -1.84 V vs. Fc^+/Fc , in MeCN, DMF and THF, respectively. These were obtained by combining the reference gas-phase electron affinity for phenyl radical from the explicitly correlated coupled-cluster method (CC) with the SMD solvation free energies of $\text{Ph}^{\bullet}/\text{Ph}^-$ at the DFT level. The differences between CC-based and purely DFT redox potentials were below 0.1 V. Using a solvation model with mixed implicit/partially explicit treatment of the coordinating solvent allowed the calculation (at the DFT level) of the standard oxidation potential of phenyllithium in THF, -0.93 V vs. Fc^+/Fc , which reflects a strong effect of Li^+ . The substitution of just one explicit molecule of ether solvent by hexamethylphosphoramide (HMPA) shifts this potential cathodically by 0.13 V.

Keywords: Phenyl radical, redox potential calculation, phenyllithium, DFT calculations, coupled cluster calculations, explicit solvation

1. Introduction

Computational chemistry provides electrochemists with powerful tools to predict redox potentials [1]. These, along with experimentally measured data, are increasingly used by organic chemists to unveil reaction mechanisms and to foresee the course of reactions, which may quicken achieving synthetic goals [2]. Moreover, activation barriers derived from voltammetric studies, under certain conditions are directly associated with reorganisation energies calculable from quantum chemical modelling [3]. The knowledge of these may be critical for organic chemists where a thermodynamically unfavourable reaction may rather occur because of a high energy barrier for a competing thermodynamically favourable path.

One of often cited values obtained from electrochemical data is the redox potential of phenyl radical/anion pair ($E^0 = 0.05$ V vs. SCE in acetonitrile) [4]. This value is based on modelling a voltammogram of benzenediazonium cation reduction, the second cathodic wave of which is interpreted as due to Ph^{\bullet} reduction. However, comparison of voltammetry curves of the same or similar systems, in which this second wave is not seen [5], in systems undergoing consecutive reactions (grafting), where less phenyl radical should be available for reduction [6], raises doubts about this interpretation. It is also inconsistent with the experimentally measured potential of C_6Br_5^- oxidation in DMF, -0.27 V vs. Fc^+/Fc ($+0.19$ vs. SCE), which was confirmed by quantum chemical calculations [7]. But five bromine atoms are expected to shift the potential much more than by 140 mV. Nonetheless, through lack of a better choice, this improbably high $E_{\text{Ph}^{\bullet}/\text{Ph}^-}^0$ value has been used in

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