Benchmark Calculations of Absolute Reduction Potential of Ferricinium/Ferrocene Couple in Nonaqueous Solutions

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Abstract: High-level ab initio molecular orbital theory is used to obtain benchmark values for the ferricinium/ferrocene (Fc\(^{++}\)/Fc) couple, the IUPAC recommended reference electrode for nonaqueous solution. The gas-phase ionization energy of ferrocene is calculated using the high-level composite method, G3(MP2)-RAD, and two higher-level variants of this method. These latter methods incorporate corrections for core correlation and, in the case of the highest level considered, use (RO)CCSD(T)/6-311+G(d,p) in place of (RO)CCSD(T)/6-31G(d) as the base level of theory. All methods provide good agreement with one another and the corresponding experimental values. Solvation energies have been calculated using PCM, CPCM, SMD, and COSMO-RS. Using G3(MP2)-RAD-Full-TZ gas-phase energies and COSMO-RS solvation energies, the absolute redox potentials of the Fc\(^{++}\)/Fc couple have been calculated as 4.988, 4.927, and 5.043 V in acetonitrile, 1,2-dichloroethane, and dimethylsulfoxide solutions, respectively.

1. Introduction

In contrast to aqueous solution, the method of measuring electrode potentials has not been well established in nonaqueous solutions.\(^1\) One of the serious problems faced is the choice of the reference electrode. For nonaqueous solutions, there is no primary reference electrode equivalent to the aqueous standard hydrogen electrode (SHE) and no general reference electrode as reliable as the aqueous reference electrodes. Although aqueous reference electrodes are often used for nonaqueous systems, the liquid junction potential (LJP) between the aqueous and nonaqueous solutions can affect the measured potentials.\(^2\) As a result, the IUPAC Commission on Electrochemistry has proposed that the ferricium/ferrocene (Fc\(^{++}\)/Fc) couple be used as an internal reference for reporting electrode potentials in nonaqueous solutions.\(^3\)

Recently, theoretical investigation of redox potentials of compounds in aqueous and nonaqueous solutions has attracted attention.\(^3\)\(^{-12}\) Computational chemistry offers an attractive alternative to experimentation, particularly in situations when experimental measurements are difficult due to the participation of other chemical reactions, or when it is necessary to clarify the role of individual reactions involved in the electrochemical processes. To date, the calculated redox potentials of nonaqueous solutions are typically reported versus an aqueous reference electrode and compared with the available experimental values.\(^5,6\) To be consistent with IUPAC recommendations, however, the calculated electrode potentials should be reported versus the Fc\(^{++}\)/Fc couple. Therefore, knowledge of the absolute reduction potential of this couple in nonaqueous solutions is necessary. Su and Girault have reported a value of 5.01 V for the absolute reduction potential for the Fc\(^{++}\)/Fc couple in 1,2-dichloroethane,\(^10\) which was compared with the value of 5.08 V as obtained from the sum of the corresponding aqueous SHE potential (4.44 V) and a correction of 0.64 V. It is worth noting that the absolute reduction potential of SHE might be different than 4.44 V, as it has been recently estimated as 4.24 and 4.27 V.\(^7,13\) In any case, the use of aqueous values of the SHE and SCE potentials to reproduce the redox potential of the Fc\(^{++}\)/Fc couple in a nonaqueous solution is problematic. Computationally, the relative redox potential of ferrocene in acetonitrile has been studied by Baik...
and Friesner, who used the Saturated Calomel Eletrode (SCE) as the reference electrode, and Roy et al., who used SHE as the reference electrode. However, converting these values to the corresponding absolute potentials is again hampered by the difficulty in estimating the relevant liquid junction potential. Moreover, the absolute values of the reduction potentials for the FeC+/Fe couple in most other nonaqueous solutions are not known, and relating theoretical and experimental redox potentials is an ongoing problem.

In the present work, we use high-level ab initio molecular orbital theory to calculate an accurate value for the absolute redox potential of the FeC+/Fc couple in several common nonaqueous solvents: acetonitrile (AN), 1,2-dichloroethane (DCE), and dimethylsulfoxide (DMSO). The accurate theoretical values reported here can be used widely in order to calculate the relative reduction potential of other species vs the FeC+/Fc couple in nonaqueous solution.

2. Computational Methods

The geometries of studied species were optimized at the B3-LYP level of theory using the LanL2DZ, LanL2TZ, TZQ, and aug-cc-pVTZ-DK basis sets for the Fe atom and the 6-31G(d) and 6-311+G(d,p) basis sets for C and H. Single-point energies were calculated using the high-level composite method G3(MP2)-RAD. This method approximates (RO)CCSD(T, FC) with the large triple-ζ basis set GTMP2large as the sum of the corresponding (RO)CCSD(T, FC)/6-31G(d) calculations and a basis set correction term, evaluated at the ROMP2 level of theory. This procedure is normally considered to achieve “chemical accuracy” (ca. 0.05 eV) for gas-phase organic thermochemistry. However, since the present compounds contain atransition metal, we also considered two improved versions of this method. In the first, which we refer to as G3(MP2)-RAD-Full, we added an additional correction for core correlation, evaluated as the difference of corresponding calculations at the (RO)CCSD(T, Full)/6-31G(d) and (RO)CCSD(T, FC)/6-31G(d) levels. In the second, we used (RO)CCSD(T, FC)/6-311+G(d,p) as our highest level of theory, so that the ROMP2 basis set correction to GTMP2large was much less significant. We refer to this method, which also included the core correlation corrections, as G3(MP2)-RAD-Full-TZ. Further details, including all component calculations, are provided in the Supporting Information.

Gas-phase zero-point energies, thermal corrections, and entropic corrections were calculated using the standard formulas for the statistical thermodynamics of an ideal gas under the harmonic oscillator approximation using the optimized geometries and scaled B3-LYP/6-31G(d)/

Table 1. Principal Geometric Parameters of Fc

<table>
<thead>
<tr>
<th>bond</th>
<th>LanL2DZ&lt;sup&gt;a&lt;/sup&gt;</th>
<th>TZQ&lt;sup&gt;a&lt;/sup&gt;</th>
<th>aug-cc-pVTZ-DK&lt;sup&gt;a&lt;/sup&gt;</th>
<th>LanL2TZ&lt;sup&gt;b&lt;/sup&gt;</th>
<th>LanL2TZ&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Experiment&lt;sup&gt;24&lt;/sup&gt;</th>
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<tbody>
<tr>
<td>Fe–C</td>
<td>1.69</td>
<td>1.68</td>
<td>1.68</td>
<td>1.68</td>
<td>1.68</td>
<td>1.66</td>
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<tr>
<td>Fe–C</td>
<td>2.08</td>
<td>2.07</td>
<td>2.08</td>
<td>2.07</td>
<td>2.07</td>
<td>2.06</td>
</tr>
<tr>
<td>C–C</td>
<td>1.43</td>
<td>1.43</td>
<td>1.43</td>
<td>1.43</td>
<td>1.43</td>
<td>1.44</td>
</tr>
<tr>
<td>C–H</td>
<td>1.08</td>
<td>1.08</td>
<td>1.08</td>
<td>1.08</td>
<td>1.08</td>
<td>1.10</td>
</tr>
</tbody>
</table>

<sup>a</sup> 6-31G(d) basis set has been used for all H and C atoms. <sup>b</sup> 6-311+G(d,p) basis set has been used for all H and C atoms.

Figure 1. Optimized structure of (a) ferrocene and (b) the ferricinium ion.

LanL2TZ frequencies. However, for the low barrier rotation of the Cp rings, the thermal and entropic corrections were calculated using the standard free rotor model formulas. Solvation energies of the studied species in the various solvents were calculated using PCM and COSMO-RS continuum models, calculated using UAKS radii at the recommended level of theory, B3LYP/6-31+G(d,p). Calculations were also performed using the recently introduced solvation models, SMD and COSMO-RS, at the B3LYP/6-31G(d) and BP/TZP levels of theory, respectively. In all solvation energy calculations, the LanL2TZ basis set was used for Fe. The default values of Klamt and the SMD-Coulomb atomic radii have been used for COSMO-RS and SMD, respectively. Since Fe was not present in the original parameterization sets for either of these models, the default SMD-Coulomb settings revert to the UAKS radius for Fe (1.456 Å), while the default COSMO-RS settings revert to the Allinger radius for Fe (1.858 Å). While neither of these values have been optimized for their respective models, this is not likely to cause a significant error in this system since the Fe atom is shielded by the two ligands.

All calculations were carried out using Gaussian 03 except for the (RO)CCSD(T) calculations, which were carried out using Gaussian 09, and the COSMO-RS calculations, which were performed using ADF software.

3. Results and Discussion

Geometries. Table 1 shows the optimized selected bond lengths of Fe using different basis sets for the Fe atom along with the corresponding literature values. The geometry is relatively insensitive to the level of theory used, though, not surprisingly, the larger basis sets for Fe give slightly better results for the Cp–Fe distance than LanL2DZ. Figure 1 shows the optimized geometry of Fe and Fe+ calculated at the level of B3-LYP using LanL2TZf for Fe and 6-31G(d) for H and C atoms. As shown in this figure, the bond length
Calculations of Absolute Reduction Potential

<table>
<thead>
<tr>
<th>Table 2. Adiabatic Ionization Energy of Fe$^a$</th>
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<tr>
<td>method</td>
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<tr>
<td>G3(MP2)-RAD</td>
</tr>
<tr>
<td>G3(MP2)-RAD-Full$^b$</td>
</tr>
<tr>
<td>G3(MP2)-RAD-Full-TZ$^{b,c}$</td>
</tr>
<tr>
<td>exp. values$^{36}$</td>
</tr>
</tbody>
</table>

$^a$ Single-point energy calculations performed using the geometries optimized at the B3-LYP/6-31G(d)/LanL2TZ level. Unless otherwise noted, the triple-$\zeta$ LanL2TZ basis set is used for Fe in all of the improved energy calculations. Computational results are shown to the nearest 0.001 eV to indicate the level of precision in the calculations; the likely level of accuracy is ca. 0.05 eV.

Adiabatic Ionization Energy. To calculate the redox potential for the Fe$^{+}$/Fc couple, we first require the gas-phase ionization energy of Fe. Surprisingly, the literature values reported for the ionization energy of Fe cover a wide range, from 6.6 to 7.2 eV (a difference of 0.6 eV or 16 kcal mol$^{-1}$).$^{36}$ We first used the high-level composite ab initio method G3(MP2)-RAD to calculate the adiabatic ionization energy (see Table 2). In applying this method, we used the triple-$\zeta$ basis set LanL2TZf for Fe in all steps of the calculation. As noted in the Computational Methods section, we also considered two improved versions of this method, G3(MP2)-RAD-Full and G3(MP2)-RAD-Full-TZ. Both of these methods include an additional correction for core correlation, and the latter method also uses (RO)CCSD(T,Fc)/6-311+G(d,p) as the base level of theory in place of (RO)CCSD(T,Fc)/6-31G(d). These improved procedures deliver results that differ from the standard G3(MP2)-RAD calculations by 0.015 eV or less, which provides a good indication that the results have converged. In particular, it is worth noting that the effect of core correlation, often important for a complete description of transition metal chemistry, is negligible (ca. 0.005 eV) for this system. The G3(MP2)-RAD-Full-TZ ionization energy (IE = 7.046 eV), which is used for the remainder of this work, falls well within the scatter of the experimental values (6.6–7.2 eV) but is slightly higher than the currently recommended values of 6.71 ± 0.08 eV and 6.81 ± 0.07 eV.$^{36,37}$

Standard Reduction Potential of Fe$^{+}$/Fc Couple. Upon reduction, the ferricinium radical cation gains one electron and converts into its reduced form, ferrocene:

$$\text{Fe(C}_2\text{H}_3)_2^+(\text{soln}) + e^- (\text{gas}) \rightarrow \text{Fe(C}_2\text{H}_3)_2(\text{soln})$$

### Scheme 1. Thermodynamic Cycle Used to Calculate Gibbs Free Energy of Reaction 1

![Scheme 1](image)

The total change in the Gibbs free energy of reaction 1 in solution, $\Delta G^o(\text{soln})$, is related to $E^o$ according to eq 2.$^{38}$

$$E^o = -\Delta G^o(\text{soln})/nF$$

where $n$ is number of electrons transferred ($n = 1$ in this case) and $F$ is the Faraday constant (23,061 kcal mol$^{-1}$ V$^{-1}$ or 96 485 C mol$^{-1}$).$^{38}$ To calculate $\Delta G^o(\text{soln})$, we have used the thermodynamic cycle shown in Scheme 1, which results in eq 3.

$$\Delta G^o(\text{soln}) = \Delta G^o(\text{gas}) + \Delta G^o(\text{solv}, \text{Fc}) - \Delta G^o(\text{solv}, \text{Fe})$$

where $\Delta G^o(\text{gas})$ is the change of standard Gibbs free of reaction 1 in the gas phase, and $\Delta G^o(\text{solv}, \text{Fc})$ and $\Delta G^o(\text{solv}, \text{Fe})$ are standard solvation energies of Fe and Fe$^+$, respectively. $\Delta G^o(\text{gas})$ can be calculated using the adiabatic IE of Fe via eq 4:

$$\Delta G^o(\text{gas}) = \Delta H^o(\text{gas}) - T\Delta S^o(\text{gas}) = -\text{IE} + \text{TC} - T\Delta S^o(\text{gas})$$

where TC is the thermal correction to the enthalpy and $\Delta S^o(\text{gas})$ is the change of entropy of the studied reaction. The thermal corrections and entropies have been calculated at the B3LYP/6-31G(d)/LanL2TZf level, and the results are tabulated in the Supporting Information. The contribution of $\Delta S^o(\text{gas})$ is $-0.108$ eV, including the entropy of free electrons (5.43 cal mol$^{-1}$ K$^{-1}$),$^{39}$ and the contribution of TC has been calculated as $-0.040$ eV, including the correction for the enthalpy of free electrons$^{39}$ at 298 K; therefore, $\Delta G^o(\text{gas})$ is $-6.979$ eV or $-160.9$ kcal mol$^{-1}$. If we instead exclude the enthalpy and entropy of free electrons, following the “ion convention” (IC),$^{39}$ a value of $-7.016$ eV or $-161.8$ kcal mol$^{-1}$ for $\Delta G^o(\text{gas})$ of the reaction is obtained instead. The difference between these two results is negligible; for the remainder of this work, we have adopted the electron convention based on Fermi–Dirac statistics (EC-FD), recommended by Bartmess.$^{39}$

As shown by eq 3, Gibbs energies of solvation of both Fe and Fe$^+$ are required in order to calculate the total change of Gibbs energy of reaction 1. Solvation energies are calculated using PCM and CPCM models of solvation together with recent models of COSMO-RS and SMD.$^{26–29}$ The results, which are summarized in Table 3, show that PCM and CPCM models predict solvation energies for Fe in acetonitrile that are positive. Since Fe dissolves in acetonitrile, this is not physically realistic. In contrast, the calculated solvation energies of Fe obtained by COSMO-RS ($-7.47$ kcal mol$^{-1}$) and SMD ($-8.50$ kcal mol$^{-1}$) are...
Table 3. Solvation Energies of Fe and Fe$^+$ in Nonaqueous Solutions of Acetonitrile (AN), 1,2-Dichloroethane (DCE), and Dimethylsulfoxide (DMSO)

<table>
<thead>
<tr>
<th>solvent</th>
<th>model</th>
<th>$\Delta G)$</th>
<th>kcal mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN</td>
<td>PCM</td>
<td>1.31</td>
<td>40.37</td>
</tr>
<tr>
<td>AN</td>
<td>CPCM</td>
<td>1.25</td>
<td>40.40</td>
</tr>
<tr>
<td>AN</td>
<td>COSMO-RS</td>
<td>-7.47</td>
<td>-53.38</td>
</tr>
<tr>
<td>AN</td>
<td>SMD</td>
<td>-5.80</td>
<td>-54.97</td>
</tr>
<tr>
<td>AN</td>
<td>experiment$^b$</td>
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<td></td>
</tr>
<tr>
<td>DCE</td>
<td>SMD</td>
<td>-8.73</td>
<td>-52.01</td>
</tr>
<tr>
<td>DMSO</td>
<td>SMD</td>
<td>-6.03</td>
<td>-52.77</td>
</tr>
</tbody>
</table>

$^a$ Solvation energies for PCM and CPCM have been calculated using UA$k$S radii at the B3LYP/6-31+G(d,p)/LanL2TZf level and for SMD and COSMO-RS using their respective default radii at the B3LYP/6-31G(d)/LanL2TZf and BP/TZP levels, respectively.

$^b$ Values of the reduction potential of Fe$^+$/Fe couple in most common nonaqueous solutions.

4. Conclusion

The absolute redox potentials of the Fe$^+/Fe$ couple in nonaqueous solutions of AN, DCE, and DMSO have been calculated as 4.988, 4.927, and 5.043 V and benchmarked against available experimental data for all components of the calculation. These values will allow for the calculation of the redox potentials of other species relative to the Fe$^+/Fe$ reference couple in most common nonaqueous solutions.$^{42}$

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Supporting Information Available: B3-LYP/6-31G(d)/LanL2TZf optimized geometries and corresponding total energies, thermal corrections, and entropies at the various levels of theory studied. This material is available free of charge via the Internet at http://pubs.acs.org.

References

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