

Benchmark Calculations of Absolute Reduction Potential of Ferricenium/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 ferricenium/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 ferricenium/ferrocene (Fc^+/Fc) couple be used 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.^{4–12} 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

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Table 1. Principal Geometric Parameters of Fc

bond	bond length (Å)					
	LanL2DZ ^a	TZQ ^a	aug-cc-pVTZ-DK ^a	LanL2TZf ^a	LanL2TZf ^b	Experiment ³⁴
Fe–Cp	1.69	1.68	1.68	1.68	1.68	1.66
Fe–C	2.08	2.07	2.08	2.07	2.07	2.06
C–C	1.43	1.43	1.43	1.43	1.43	1.44
C–H	1.08	1.08	1.08	1.08	1.08	1.10

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

and Friesner,¹⁴ who used the Saturated Calomel Electrode (SCE) as the reference electrode, and Roy et al.,¹⁵ 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 Fc⁺/Fc 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 Fc⁺/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 Fc⁺/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,¹⁶ LanL2TZf,^{17,18} TZQ,¹⁹ and aug-cc-pVTZ-DK²⁰ 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.^{21,22} 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.^{21,22} However, since the present compounds contain a transition 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 scaled²³ B3-LYP/6-31G(d)/

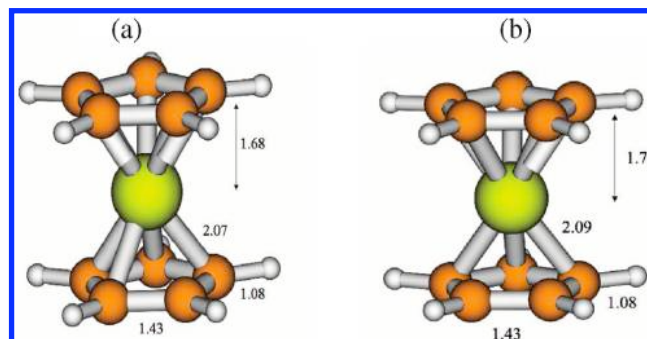


Figure 1. Optimized structure of (a) ferrocene and (b) the ferricinium ion.

LanL2TZf 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 CPCM continuum models^{24,25} calculated using UAKS radii at the recommended²⁶ level of theory, B3LYP/6-31+G(d,p). Calculations were also performed using the recently introduced solvation models, SMD²⁷ and COSMO-RS,^{28,29} at the B3LYP/6-31G(d) and BP/TZP levels of theory, respectively. In all solvation energy calculations, the LanL2TZf basis set was used for Fe. The default values of Klami^{28,29} and the SMD-Coulomb atomic radii²⁷ have been used for COSMO-RS and SMD, respectively. Since Fe was not present in the original parametrization 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 03³⁰ except for the (RO)CCSD(T) calculations, which were carried out using Gaussian 09,³¹ and the COSMO-RS calculations, which were performed using ADF^{32,33} software.

3. Results and Discussion

Geometries. Table 1 shows the optimized selected bond lengths of Fc using different basis sets for the Fe atom along with the corresponding literature values.³⁴ 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 Fc and Fc⁺ 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

Table 2. Adiabatic Ionization Energy of Fc^a

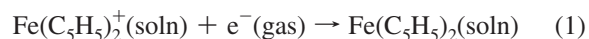
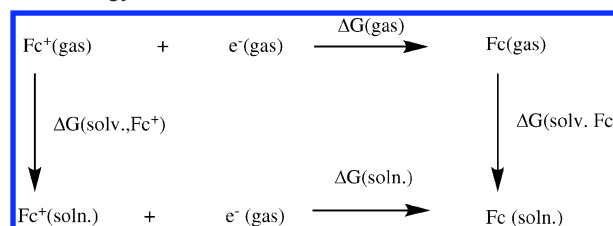
method	IE (0K) eV
G3(MP2)-RAD	7.062
G3(MP2)-RAD-Full ^b	7.067
G3(MP2)-RAD-Full-TZ ^{b,c}	7.047
exp. values ³⁶	6.6–7.2

^a Single-point energy calculations performed using the geometries optimized at the B3-LYP/6-31G(d)/LanL2TZf level. Unless otherwise noted, the triple- ζ LanL2TZf 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. ^b Includes an additional correction for core correlation, using the (RO)CCSD(T,Full)/6-31G(d)/LanL2TZf level of theory. ^c (RO)CCSD(T)/6-311+G(d,p) has been used as the base level of theory in this method; see the Computational Methods section and Supporting Information for more details.

of Fe–C in Fc⁺, 2.09 Å, is longer than the corresponding bond length in Fc, 2.07 Å, which is in perfect agreement with the experiment.³⁴ Thus, removal of an electron from the bonding orbital of Fc leads to an increase of the Fe–Cp distance, suggesting that the strength of the Fe–C bond has been reduced. Although one might expect that the staggered isomer (*D*_{5d}) is more favorable, the equilibrium conformation in the gas phase is the eclipsed (*D*_{5h}) form, and this is in agreement with previous experimental and theoretical studies.³⁵

Adiabatic Ionization Energy. To calculate the redox potential for the Fc⁺/Fc couple, we first require the gas-phase ionization energy of Fc. Surprisingly, the literature values reported for the ionization energy of Fc 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- ζ 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 Fc⁺/Fc Couple. Upon reduction, the ferricinium radical cation gains one electron and converts into its reduced form, ferrocene:

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

The total change in the Gibbs free energy of reaction 1 in solution, ΔG (soln), is related to E according to eq 2:³⁸

$$E = -\Delta G(\text{soln})/nF \quad (2)$$

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 ΔG (soln), we have used the thermodynamic cycle shown in Scheme 1, which results in eq 3.

$$\Delta G(\text{soln}) = \Delta G(\text{gas}) + \Delta G(\text{soln}, \text{Fc}) - \Delta G(\text{soln}, \text{Fc}^+) \quad (3)$$

where ΔG (gas) is the change of standard Gibbs free of reaction 1 in the gas phase, and ΔG (soln., Fc) and ΔG (soln., Fc⁺) are standard solvation energies of Fc and Fc⁺, respectively. ΔG (gas) can be calculated using the adiabatic IE of Fc via eq 4:

$$\Delta G(\text{gas}) = \Delta H(\text{gas}) - T\Delta S(\text{gas}) = -\text{IE} + \text{TC} - T\Delta S(\text{gas}) \quad (4)$$

where TC is the thermal correction to the enthalpy and ΔS (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 $T\Delta S$ (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 electrons³⁹ at 298 K; therefore, ΔG (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 ΔG (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 Fc and Fc⁺ 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 Fc in acetonitrile that are positive. Since Fc dissolves in acetonitrile, this is not physically realistic. In contrast, the calculated solvation energies of Fc obtained by COSMO-RS (-7.47 kcal mol⁻¹) and SMD (-8.50 kcal mol⁻¹) are

Table 3. Solvation Energies of Fc and Fc⁺ in Nonaqueous Solutions of Acetonitrile (AN), 1,2-Dichloroethane (DCE), and Dimethylsulfoxide (DMSO)

solvent	model	ΔG (solv.) ^a kcal mol ⁻¹	
		Fc	Fc ⁺
AN	PCM	+1.31	-40.37
AN	CPCM	+1.25	-40.40
AN	COSMO-RS	-7.47	-53.38
AN	SMD	-8.50	-54.97
AN	experiment ⁴⁰	-7.65	
DCE	SMD	-8.73	-52.01
DMSO	SMD	-6.03	-52.77

^a Solvation energies for PCM and CPCM have been calculated using UAKS 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.

Table 4. Absolute Reduction Potentials (V) of the Fc⁺/Fc Couple in Nonaqueous Solution^a

solvent model	solvent		
	AN	DCE	DMSO
COSMO-RS	4.988	4.927	5.043
SMD	4.964	5.102	4.952
experiment	4.980 ^b	5.01 ^c	

^a Calculated at the G3(MP2)-RAD-Full-TZ level using various solvation methods as shown. Computational results are shown to the nearest 0.001 V to indicate the level of precision in the calculations; the likely level of accuracy is ca. 0.05–0.1 V. ^b Calculated from the experimental⁴¹ value of 0.380 V for the reduction potential of Fc⁺/Fc in acetonitrile relative to the Saturated Calomel Electrode (SCE), taking into account a recent value⁹ of 4.60 V for SCE in acetonitrile. ^c From ref 10.

negative and are in excellent agreement with experimental results (-7.65 kcal mol⁻¹).⁴⁰

Using G3(MP2)-RAD gas-phase energies together with the COSMO-RS and SMD solvation energies, the absolute values of the reduction potential of the Fc⁺/Fc couple in AN, DCE, and DMSO have been calculated and are shown in Table 4. Both sets of values are in excellent agreement with the available experimental data,^{10,41} with the COSMO-RS results marginally closer overall. As a final test of these numbers, we have previously used G3(MP2)-RAD to calculate the absolute redox potential of *para*-benzoquinone in acetonitrile.⁹ This absolute value (4.04 V) can now be combined with our new absolute value of the Fc⁺/Fc couple in the same solvent to obtain a theoretical value for the relative redox potential of this compound in acetonitrile. The values obtained (-0.948 or -0.924 V, depending on whether the SMD or COSMO-RS results are used for the reference electrode) both compare well with the experimental value for the same system (-0.851 V),⁸ with relatively small deviations of 0.097 and 0.073 V, respectively.

4. Conclusion

The absolute redox potentials of the Fc⁺/Fc 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 Fc⁺/Fc 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>.

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