Redox Potentials of Ligands and Complexes – a DFT Approach

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ABSTRACT

A review of the limited literature concerned with theoretical ways to predict experimentally measured redox potentials of ligands and complexes is presented. Electrochemical and related DFT studies involving series of *para*-substituted nitrobenzenes and β-diketone bidentate ligands are discussed. New studies involving ferrocenes and bimetallic complexes (containing both rhodium and iron) are additionally reported. Correlations of redox potentials with calculated descriptors; electron affinity (EA), group electronegativity (χ_R), electrophilicity index (ω), LUMO energy (E_{LUMO}) and HOMO energy (E_{HOMO}) – obtained from calculated electronic energies of neutral, anionic and cationic molecules, are compared. Observed $E^{0'}$, E_{pa} or E_{pc} gave excellent correlations in the linear relationships between E_{pc} and E_{LUMO} ($R^2 > 0.99$), and E_{pa} and E_{HOMO} ($R^2 > 0.92$). Close correlation with the HOMO-1 energy was also found with the ferrocene-based second oxidation in the Rh complex.

1. Introduction

A variety of definitions had been invented to describe and quantify the direct or indirect effect and/or strength of electron-withdrawing and donating substituents in molecules. Following are some of these definitions that are of particular importance in computational chemistry.

Electron affinity (EA) of an atom or molecule is the associated energy change that occurs when an electron is added to the neutral species to form a negative ion,[1] while ionization potential (IP) is the energy required to remove an electron from an atom, radical, or molecule.

The global electrophilicity index (ω) representing the electrophilic power of atoms and molecules, as defined by Parr and coworkers,[2] depends on both EA and IP.

In 'group electronegativity' (χ_R) electronegativity is associated more with different functional groups than with individual atoms.[3,4]

Lastly, theoretically computed HOMO or LUMO energies of molecules are closely associated with the respective oxidation and reduction potentials of molecules.[5]

Experimental oxidation and reduction potentials are obtained by means of cyclic voltammetry (CV), which is by far the most effective electro-analytical technique for the study of electro-active species. Peak separation in CVs is given by, $\Delta E_p = E_{pa} - E_{pc}$, where E_{pa} and E_{pc} are the respective peak potentials of anodic and cathodic scans associated with an electrochemical process. The formal reduction potential is defined as, $E^{0'} = (E_{pa} - E_{pc})/2$. A redox couple is said to be electrochemically reversible if the difference in peak potential (ΔE_p) is 59 mV at 25 °C for one electron transfer processes. Because of slow transfer kinetics at the electrode surface, over-potentials and high solvent resistance, the peak separation increases to above 59 mV and values up to 90 mV can be considered as electrochemically reversible. A redox

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couple is said to be chemically reversible if i_{pa}/i_{pc} is equal to unity. A peak separation of 90 mV $\leq \Delta E_p \leq$ 150 mV is considered quasi-reversible, while $\Delta E_p > 150$ mV indicates electrochemically irreversible behaviour. A chemically irreversible system is where only reduction or oxidation can occur.

To different extents the former definitions have been related to experimentally observed oxidation and reduction potentials. Amongst these, some of the best results were obtained by correlating EA with one-electron reduction potentials. Hicks *et al.* computed EAs for a set of 29 mono-substituted benzalacetophenones (chalcones), utilizing the B3LYP/6-31G* functional. A correlation coefficient of 0.969 in the linear relation with experimental formal reduction potentials ($E^{0'}$) was found.[6] Bateni *et al.* did an EA DFT study of 19 metal-salen compounds ($R^2 = 0.93$). Experimental reduction potentials of 14 different metal-salens were correctly predicted by the latter relationship with a mean unsigned error of 99 mV.[7] Zubatyuk *et al.* found the mPWB1K/TZVP computational method to be providing the most accurate EA results for calculation of one-electron reduction potentials of nitro-aromatic compounds, with an RMS error of 0.1 eV. Together with the PCM (Bondi) method it also gave the most accurate difference in solvation energies between neutral oxidized and anion-radical reduced forms in a series of nitro-aromatics. Compared with experimental values $E^{0'}$ was calculated with an RMS error of 0.10 V.[8] Here, theoretical calculations of $E^{0'}$ were performed in two steps, i.e. calculation of the free energy of reduction, and difference in solvation energies of oxidized and reduced forms.

In general, reduction potentials, i.e. where neutral species are turned into corresponding anions, are expected to correlate with EA, while oxidation potentials are to correlate with IP. However, in some instances, correlations of IP with reversible oxidation potentials were found to be poor.[9] Studies of both tetraalkylhydrazines[10] and 3-substituted 2-oxa-3-azabicyclo

[2.2.2]octane derivatives are examples of poor IP correlations.[11]

Employing the Hammett equation in the interpretation of redox potentials had also been reasonably successful, especially with regard to *meta* and *para* substituted species. Hammett constants for *ortho* substitution had hardly been used, largely due to failure to find good correlation as a consequence of proximity effects at the reaction centre.[12] Through the years this approach had been refined, with some reviews written on the topic.[13,14]

According to Koopman's theorem,[5] ionization energy is equal to the HOMO energy of a molecule, but of opposite sign, with the consequence that oxidation potentials may be related to HOMO energies. In the same way LUMO energy is related to reduction potentials. Both HOMO and LUMO energies may easily be calculated theoretically. A great advantage of this method is that it ignores solvation energy and that these energies are conveniently available from computational molecular geometry optimizations. Regardless the fact that Koopman's theorem was already published in 1933, practical applications in the context of this paper slowly started gaining ground only during the last decade. As Sereda *et al.*[15] in 2006 rightfully stated, 'The open-shell' nature of the reduced species and often the necessity to take into account solvation makes the prediction of redox-potentials a challenging and time consuming computational problem. However, Koopmans' theorem enabled us to relate redox-potentials of bicyclic quinones with their LUMO energies, which solely characterize the starting compound. Despite the neglected orbital relaxation that immediately follows the reduction, such correlations have proved to be an efficient tool for prediction of redox-potentials of anthracyclines,[16] substituted anthracenes,[17] and oligothiophenes.[18] A rough correlation was also found between the first reduction potentials of substituted bicyclic quinones and LUMO energies, and second reduction waves and calculated LUMO+1 energies.[15] Other related studies include semi-empirical calculations of E_{LUMO} correlated with reduction potentials of a series of chalcones ($R^2 = 0.92$),[19] and a similar study on 16 catechol derivatives.[20] For the latter, however, the *ab initio* B3LYP/6-311+G** functional was used. Correlation coefficients varying from 0.70 to 0.88 were obtained.

As a consequence of the foregoing evidence we resolved to embark on a comprehensive study to find the most suitable means to theoretically predict redox potentials. The ongoing investigation was scheduled along the logical sequence of starting with the simple and progressing towards the complex. It was thus decided to commence with a series of 12 substituted nitrobenzenes,[21] known for its well established reversible redox behaviour at the nitro group,[22,23,24] while good communication exists between this redox active centre and any of a variety of *para*-substituents. To find the most accurate theoretical method at the outset, experimental reduction potentials were correlated with a variety of DFT computed descriptors, i.e.

electron affinity (EA = E – E_{ANION}), *

ionization potential (IP = E – E_{CATION}),

calculated relative group electronegativities (χ_R = (IP + EA)/2),

global electrophilicity index ($\omega = \mu^2/2\eta$, $\mu \approx$ –(IP + EA)/2, $\eta \approx$ (IP-EA)),

and E_{HOMO} & E_{LUMO} of neutral molecules.

As additional experimental validation formal reduction potentials (E_{pc}) were also correlated with

^{1}H NMR chemical shifts,

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* Electronic energies, E, of optimized neutral, anionic and cationic molecules.

^{13}C NMR chemical shifts, and

Infra-Red N-O stretching frequencies, ν_{as}, as reported elsewhere.[21]

Based on findings from the study of the former series of simple organic compounds, the computational investigation was extended to include a series of the well known bidentate β-diketone ligand as well, see Scheme 2.[25] The ultimate goal was to also find a theoretical means to predict the effect of electronically altered ligands on the oxidation and reduction potentials of the metals it might be coordinated to. The latter study is newly reported here, and includes series of six ferrocenyl-containing β-diketones, and five ferrocenyl-containing β-diketonato(cod) rhodium(I) complexes (cod = 1,5-cyclooctadiene). The iron center in ferrocene provided the option to correlate calculated descriptors with the Fe^{II-III} transition, while the rhodium complex involves both Rh^{I-III} and Fe^{II-III} metal-centered oxidations.

2. Experimental and Computational Methods

2.1. General

Syntheses, NMR, IR and cyclic voltammetry were performed as reported earlier.[21,25,26,27]

2.2. Quantum Computational Methods

Density functional theory (DFT) calculations were performed using the PW91/TZP,[28] OLYP/TZP (Triple ζ polarized)[29,30,31,32] and the B3LYP/6-311G(d,p)[29,33] functionals and basis sets as implemented in the Amsterdam Density Functional (ADF2009)[34] and GAUSSIAN 09 packages.[35] Calculations in solution were performed using the Conductor-like Screening Model (COSMO).[36] Calculations were in gas phase unless specified otherwise.
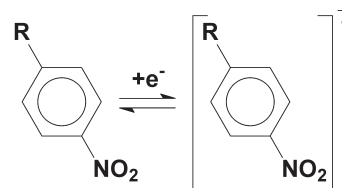
Whether artificially generated atomic coordinates or coordinates obtained from X-ray crystal data (Cambridge Structural Database)[37] were used in the input files, optimizations for each compound resulted in the same optimized geometry. No symmetry limitations were imposed during the calculations.

3. Results and Discussion

The cyclic voltammograms of a series of twelve *para*-substituted nitrobenzenes were obtained afresh, ensuring uniform conditions applied during all scans, see Fig. 1.[21] Nitrobenzene shows one reversible couple according to Scheme 1. Formal reduction potentials, $E^{0'}$, which is the average between peak oxidation and reduction potentials, are used here.

Both the 'pure' classical OLYP functional and the hybrid B3LYP functional were used to calculate energies of neutral, cationic and anionic species, from which electron affinity, electrophilicity index and relative group electronegativity for each compound were calculated. LUMO energy, E_{LUMO}, was obtained directly from geometry optimized structures without further processing. These descriptors were correlated with experimentally measured formal reduction potentials, $E^{0'}$, see Fig. 2.

Compared to related correlations referred to earlier (under Introduction), excellent agreement ($R^2 > 0.99$) between $E^{0'}$ and

Scheme 1
Reduction of *para*-substituted nitrobenzenes.

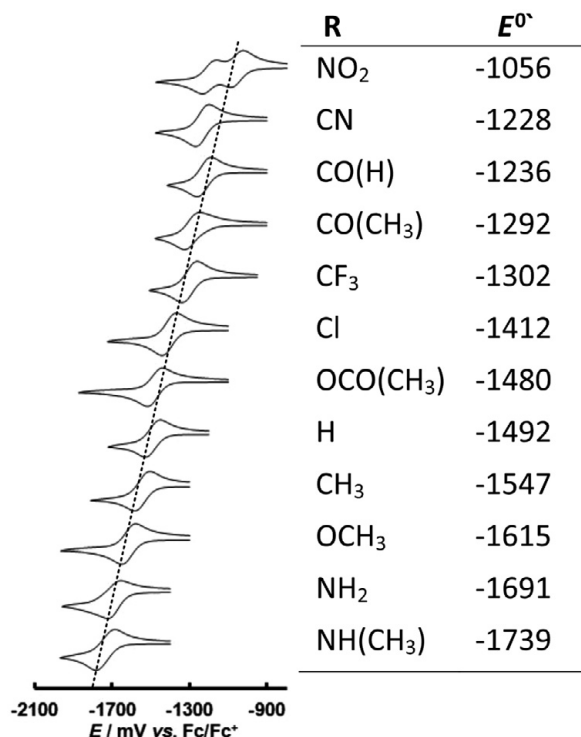| R	$E^{0'}$
NO_2	-1056
CN	-1228
CO(H)	-1236
$CO(CH_3)$	-1292
CF_3	-1302
Cl	-1412
$OCO(CH_3)$	-1480
H	-1492
CH_3	-1547
OCH_3	-1615
NH_2	-1691
$NH(CH_3)$	-1739

Figure 1 *Left*: Comparative cyclic voltammograms (*vs.* FcH/FcH$^+$) at a scan rate of 100 mV s^{-1} for the *para*-nitrobenzene series R-C$_6$H$_4$-NO$_2$ (2 mmol dm^{-3}), measured in 0.2 mol dm^{-3} [NBu$_4$][PF$_6$]/CH$_3$CN on a glassy carbon working electrode at 25 °C. The dotted line indicates the cathodic shift in E$^{0'}$ (NO$_2$). *Right*: Corresponding R groups and E$^{0'}$ potentials are shown.

the theoretical descriptors E$_{LUMO}$ and ω was obtained, which is closely followed by EA (0.98) and χ$_R$ (0.95), see Fig. 2 and Table 2. Relationships between E$_{LUMO}$, EA, ω and χ$_R$ for R-C$_6$H$_4$-NO$_2$ that result from gas-phase adiabatic calculations, and E$^{0'}$ values generally gave the best fit (Table 2). Solution phase calculations were slightly less accurate than gas phase calculations, regardless the fact that electrochemical data were obtained in solution. One reason for calculated energies being independent of solvation effects could be the fact that redox potentials tend to be independent of solvent when structurally similar substances are examined in aprotic solvents.[38]

The B3LYP functional yielded results that appear only slightly better than that obtained by the OLYP functional, see Table 1. Single point calculations on the optimized geometries of the neutral species for the anodic and cathodic species gave similar correlations for E$_{LUMO}$ *vs.* E$^{0'}$. Adiabatic, i.e. geometry relaxed calculations, gave much better results than corresponding single point calculations of ω and χ$_R$, which indicates that cation and anion geometries also have to be optimized for improved accuracy. 'Intrinsic group electronegativities' calculated by De Proft *et al.*,[44] where the EA and IP of isolated groups were calculated, correlate poorly to our formal reduction potentials (indicated in Fig. 2f). The fact that this method does not take the group's molecular environment into account results in data that does not correlate with E$^{0'}$, as opposed to what is observed by us, where the *entire* molecule is taken into consideration.

From this initial study it became evident that E$_{LUMO}$ represents the descriptor of choice, both due to best correlation and the convenience of being directly available from computational results of the neutral molecule.

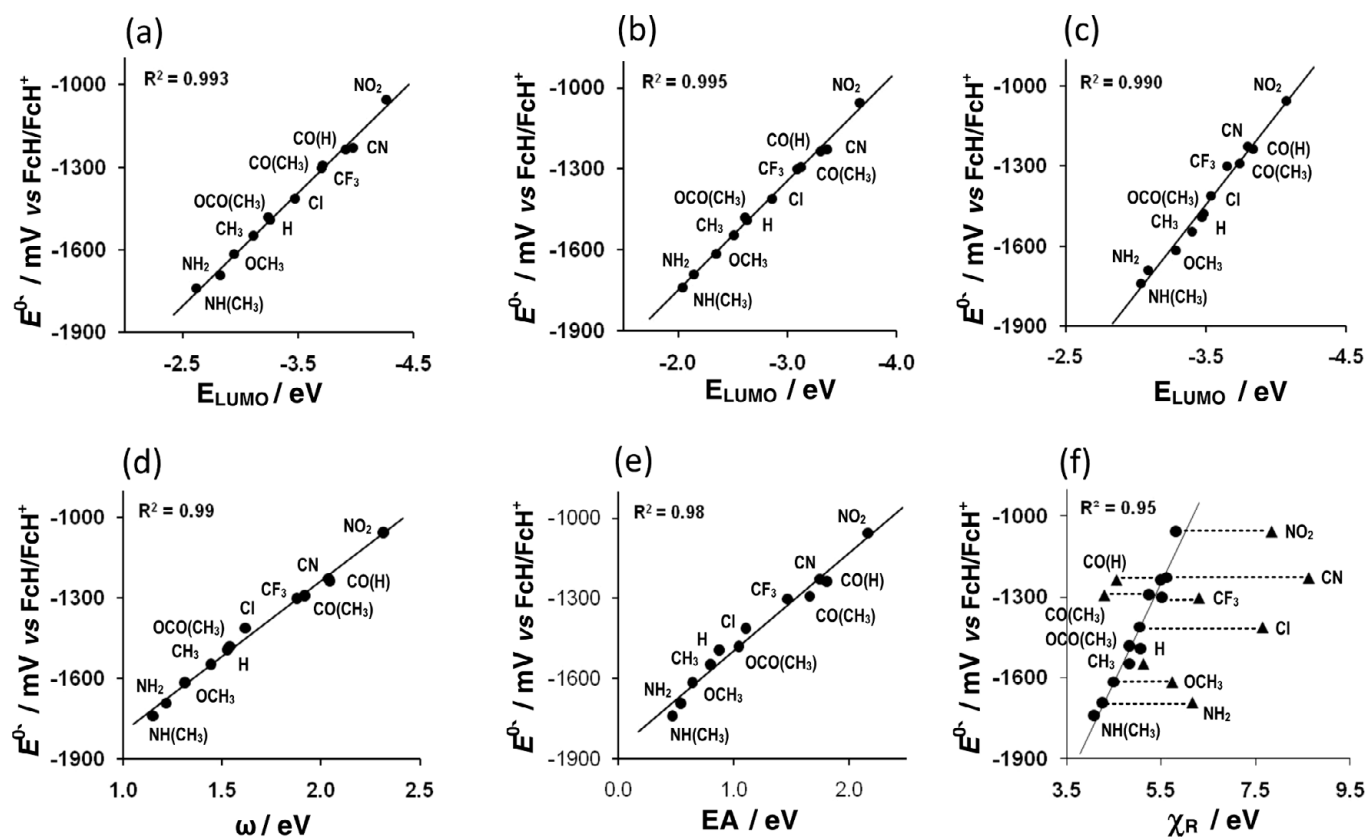Secondly, β-diketone (1,3-substituted-propane-1,3-dione) was

Figure 2 *Top*: Linear correlation graphs of the formal reduction potentials (E$^{0'}$) of R-C$_6$H$_4$-NO$_2$ and LUMO energies, using (**a**) OLYP (gas phase), (**b**) B3LYP (gas phase), and (**c**) OLYP (with solvent effects, CH$_3$CN). *Bottom*: Linear correlations of E$^{0'}$ with calculated parameters; (**d**) global electrophilicity index (ω), (**e**) electron affinity (EA) and (**f**) calculated relative group electronegativity (χ$_R$) (Calculated group electronegativities reported by De Proft *et al.* are shown as triangles: ▲).[21]

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Table 1 Linear correlation coefficients obtained from different computational methods.

Computational method	Correlation coefficient/R^2			
	E_{LUMO}	ω	EA	χ_R
B3LYP/6-311G(d,p)				
Gas phase, adiabatic	0.995	0.997	0.983	0.963
OLYP/TZP				
Gas phase, adiabatic	0.993	0.992	0.975	0.950
Gas phase, single point	0.993*	0.865	0.973	0.681
Solvent phase, adiabatic	0.990	0.876	0.974	0.885

*E_{LUMO} single point and adiabatic calculations are similar because both methods optimize
neutral species.
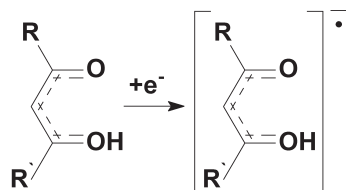
Scheme 2

Reduction of enolized β-diketones. R, R′ (E_{pc} *vs.* FcH/FcH$^+$ in V) = CF$_3$, PhNO$_2$ (–1.045), CF$_3$, CF$_3$ (–1.243), CF$_3$, Th (–1.541), CF$_3$, Ph (–1.564), CF$_3$, CH$_3$ (–1.851), CF$_3$, CMe$_3$ (–1.860), Th, Th (–1.867), Ph, Th (–1.884), Ph, Ph (–1.934) and Ph, CH$_3$ (–2.138), where PhNO$_2$ = (*p*NO$_2$–C$_6$H$_4$), Th = theonyl (C$_4$H$_3$S), Ph = phenyl (C$_6$H$_5$) and Me = methyl (CH$_3$).

employed.[25] This molecule is slightly larger than nitrobenzene, and has two groups, R and R′, which may influence reduction potentials. β-Diketones are known for more than a century[39] and give rise to rich and interesting coordination chemistry.[40,41,42] The electrochemistry of this class of compounds is well established, and is strongly influenced by substituents.[26,43] CV's of β-diketones show one electrochemically irreversible reduction peak between –1 and –2 V *vs.* FcH/FcH$^+$, see Scheme 2. The reduction potentials, E_{pc}, of ten 1,3-substituted diketone RCOCHC(OH)R′ derivatives were measured by cyclic voltammetry and used in correlations with calculated descriptors.[25]

Calculated descriptors; E_{LUMO}, EA and ω obtained from computed electronic energies of the neutral, anionic and cationic molecules were correlated with corresponding first reduction potentials, E_{pc}, see Fig. 3. Again, close to unity correlation in the linear relationship between experimental E_{pc} and calculated E_{LUMO} ($R^2 > 0.99$, see also Table 2) was found. The correlation coefficient of E_{LUMO} was followed by ω (0.94) and EA (0.84). DFT calculations were in support of experimental results in which the relative ease by which the β-diketone ligand may be

reduced is brought about by the presence of R-groups, in the order, PhNO$_2$>CF$_3$>Th>Ph>CH$_3$>CMe$_3$.[25]

Already at this early stage it became clear that the more involved method to obtain EAs is significantly less accurate in estimating reduction potentials as compared to E_{LUMO}. However, it was found that close correlations can only be obtained amongst related molecules, i.e. molecules with substituents on different phenyl positions correlate poorly if the substituent is not the same right through.[21] For this reason *ortho*- and *meta*-substituents were not included in the nitrobenzene study (Scheme 1), where it was indeed observed that correlation coefficients decrease significantly when the latter is included with the *para* series. As the aim of these investigations was to find the best possible correlations of computational with electrochemical data, it was therefore evident that different series should be treated separately.

To extend the present study with eventual aim to also include metal-centered oxidations (or reductions), a series of five ferrocenyl-containing β-diketones was employed,[26] see Scheme 3. These compounds differ by substitution at one position on the diketone moiety, varying this site from strongly electron donating ferrocenyl to strongly electron withdrawing trifluoromethyl.
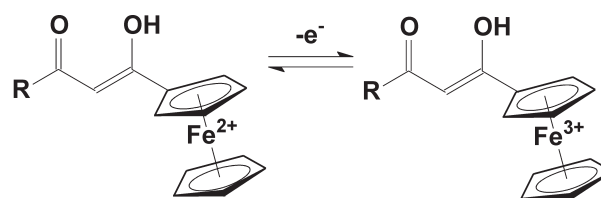
Scheme 3

Fe^{II-III} oxidation of electronically altered ferrocenyl-containing β-diketones. R ($E^{0'}$ *vs.* FcH/FcH$^+$ in mV) = CF$_3$ (317), CCl$_3$ (293), CH$_3$ (236), Ph (231), Ru (213), Fc (188).[26]
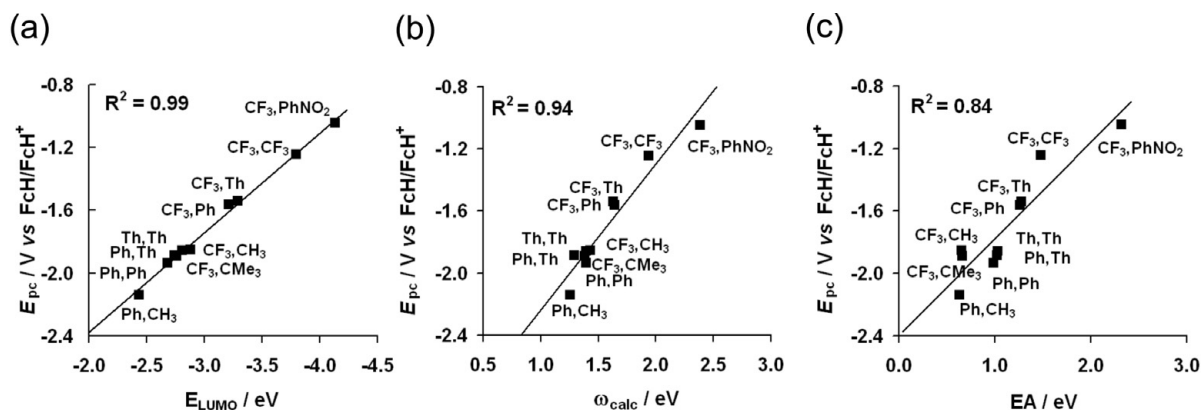
Figure 3 Linear correlation graphs of 1,3-substituted β-diketone RCOCHC(OH)R′ reduction potentials (E_{pc}) with calculated parameters (**a**) LUMO energy, (**b**) global electrophilicity index (ω), and (**c**) electron affinity (EA).[25] R and R′ are indicated on the graphs.
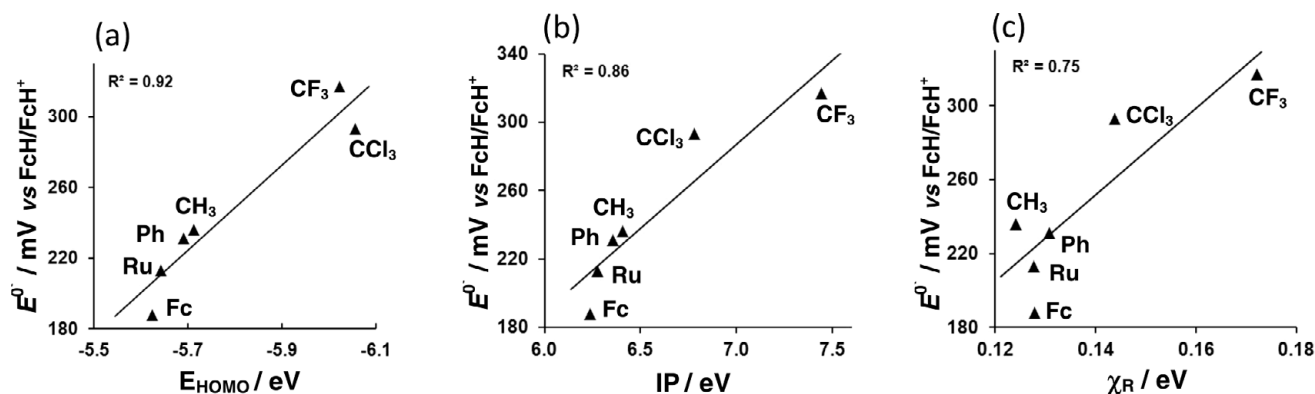
Figure 4 Linear correlations between $E^{0'}$ and (**a**) E_{HOMO}, (**b**) IP, and (**c**) χ_R, for ferrocene-containing β-diketones FcCOCHC(OH)R'.[43] R is indicated on the graphs.

Here we focus only on the reversible oxidation of the ferrocenyl group and not on the reduction of the β-diketonato ligand. Cyclic voltammetry studies on these β-diketones were formerly done as a tool to obtain group electronegativities on the Gordy scale. A linear relationship between observed group electronegativity, χ_R and E_{pa}, as well as observed carbonyl stretching frequencies of methyl esters of the type, RCOOMe, yielded average χ_R values of 1.87 for the ferrocenyl group and 2.82 for the ferrocenium group.[26]

In addition to the previous reduction potential correlations with E_{LUMO}, our investigation now also includes correlations of the $Fe^{II} \rightarrow Fe^{III}$ first oxidation potential with E_{HOMO}, as well as with the ionization potential, IP, and calculated group electronegativity using Mulliken's formula, χ_R, see Fig. 4.

A correlation coefficient of 0.92 was found for E_{HOMO}, involving the orbital from which an electron is lost during oxidation. Where as electron affinity is used in connection with reductions, ionization potential is related to the oxidation potential. This correlation, namely with IP, is somewhat worse, i.e. $R^2 = 0.87$. The global electrophilicity index was also tested but not shown here, as it gave a poor correlation ($R^2 = 0.67$).

Lastly we extended our study to complexes that contain two metals, i.e. the ferrocenyl-containing β-diketonato rhodium(I) cod complex, [Rh(FcCOCHCOR)(cod)] (cod = 1,5-cyclooctadiene, with R = CF_3, CCl_3, CH_3, Ph and Fc). Electrochemistry

of these compounds revealed irreversible oxidation at the Rh^I centre, involving a two-electron transfer process to form Rh^{III}.[27]

Figure 6 gives correlations between E_{pa} and E_{HOMO} for the $Rh^I \rightarrow Rh^{III}$ 2-electron oxidation. Consistent with previous case studies presented here, a good correlation coefficient was again found, with R^2 being 0.94. Following the two electron oxidation of Rh^I to Rh^{III} in [Rh(FcCOCHCOR)(cod)], is the oxidation of the ferrocenyl group at a slightly higher potential than the rhodium oxidation. Oxidation of the ferrocenyl group involves either removal of one of the electrons from the HOMO of rhodium(III), or from the HOMO-1 of the original rhodium(I) complex, see Scheme 4 and Fig. 5. Figure 6 (b) shows an excellent correlation between the formal oxidation potential of the ferrocenyl group in [Rh(FcCOCHCOR)(cod)]$^{2+}$ and the energy of HOMO-1 of [Rh(FcCOCHCOR)(cod)] ($R^2 = 0.98$). Figure 7 displays the HOMO of [Rh(FcCOCHCOCH$_3$)(cod)], which is computed to be

Scheme 4
$Rh^I \rightarrow Rh^{III}$ and $Fe^{II} \rightarrow Fe^{III}$ oxidation of [Rh(FcCOCHCOR)(cod)] complexes (Fc = ferrocenyl). For $Rh^I \rightarrow Rh^{III}$, R ($E_{pa}$ *vs.* FcH/FcH$^+$ in mV) = CF$_3$ (269), CCl$_3$ (265), CH$_3$ (177), C$_6$H$_5$ (184) and Fc (135). For $Fe^{II} \rightarrow Fe^{III}$, R ($E^{0'}$ *vs.* FcH/FcH$^+$ in mV) = CF$_3$ (329), CCl$_3$ (312), CH$_3$ (232), C$_6$H$_5$ (237) and Fc (203).[27]

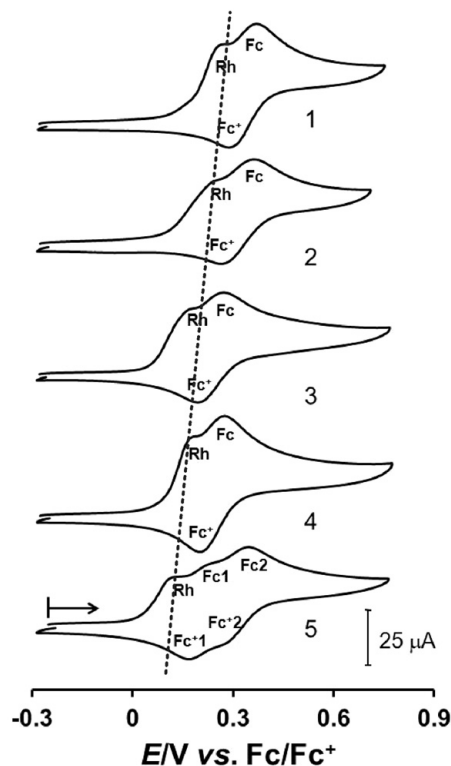**Figure 5** CVs of different [Rh(FcCOCHCOR)(cod)] complexes measured at a scan rate of 100 mV s^{-1} on a glassy carbon working electrode at 25.0(1) °C for R = CF$_3$ (**1**), CCl$_3$ (**2**), CH$_3$ (**3**), C$_6$H$_5$ (**4**) and Fc (**5**).[27] The dotted line indicates the cathodic shift in E_{pa}($Rh^{I \rightarrow III}$), and the arrow shows initial scan direction.
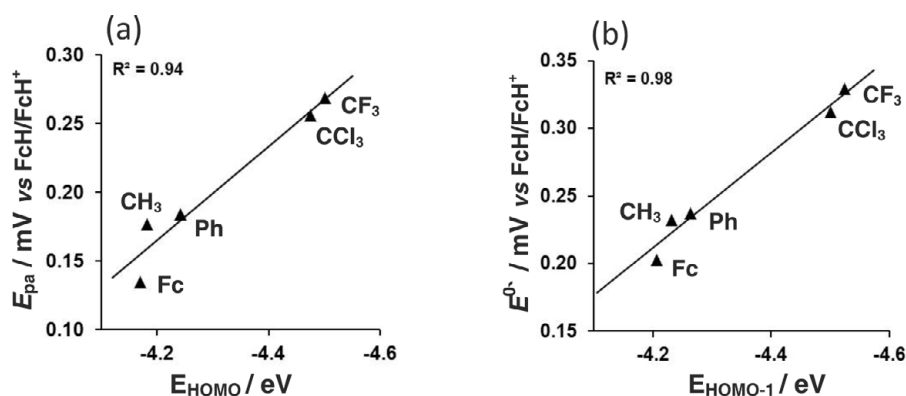
Figure 6 Linear correlations between (**a**) E_{pa} and E_{HOMO} for the first oxidation wave ($Rh^{I–III}$), and (**b**) $E^{0'}$ and E_{HOMO-1} for the second oxidation wave ($Fe^{II–III}$), for the $[Rh(FcCOCHCOR)(cod)]$ complexes. R is indicated on the graphs.
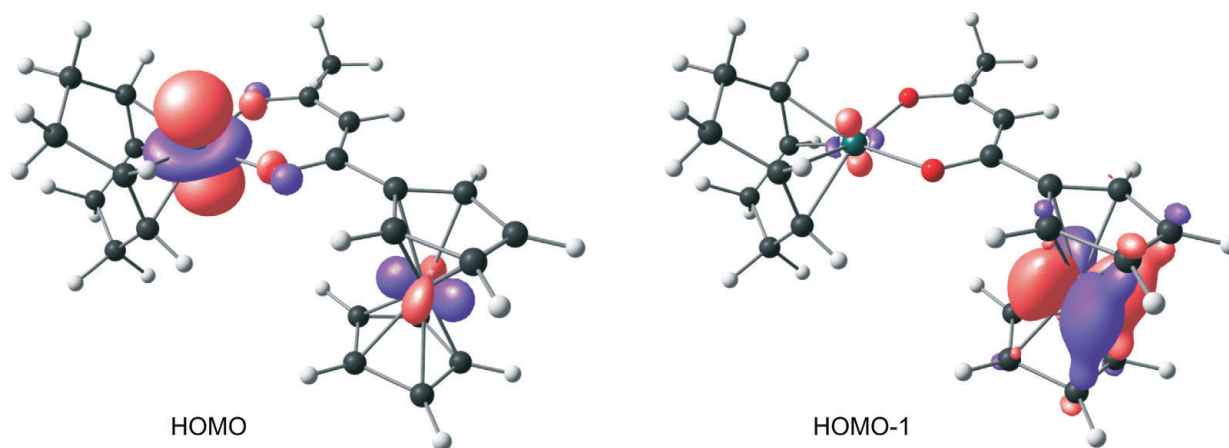

Figure 7 HOMO and HOMO-1 orbitals of $[Rh(FcCOCHCOCH_3)(cod)]$. The HOMO is mainly rhodium based and the HOMO-1 mainly Fe-based. The oxidation of $[Rh(FcCOCHCOR)(cod)]$ firstly involves removal of 2 electrons from the HOMO, followed by oxidation of Fe^{II} which involves an electron in the HOMO-1. Color scheme: C (charcoal), H (grey), O (red), Rh (green), Fe (purple).

79% rhodium based. The HOMO-1, also displayed in Fig. 7, is 77% Fe based, thus confirming the location from which the second oxidation ($Fe^{II→III}$) takes place.

Table 2 gives the linear equations of the trend lines for all correlations considered in this report. The corresponding correlation coefficients, R^2, gives an indication of the closeness of the data spread to linearity, with 1.0 representative of a perfect linear fit. The provided equations may be used to predict reduction potentials from theoretically obtained LUMO energy values, and oxidation potentials from theoretically obtained HOMO energies. This capability is anticipated to be of great aid in the pre-design (before synthesis) of molecules and complexes with specific required redox properties, without first having to work through often tedious and expensive experimental procedures.

4. Conclusion

Convincing evidence in favour of theoretically calculated orbital energies as means to predict redox potentials was presented. HOMO and LUMO energies are conveniently available from computationally optimized geometries of neutral molecules, without any additional processing. In the organic molecule studies (nitrobenzenes and β-diketones) reviewed here, correlations between first reduction potentials and LUMO energies were better than 0.99, which represents outstanding accuracies of close to unity. The Fe and Rh containing complexes yielded newly reported first oxidation potential correlations with HOMO energies better than 0.92. The HOMO-1 energy of the Rh complex, which corresponds to consequent oxidation of

Table 2 Electrochemical and DFT linear correlation equations and coefficients of four chemical series.

Series	Linear equation	R^2
Nitrobenzenes	$E^{0'} = -409.3\ E_{LUMO} - 2823$	0.99
	$E^{0'} = 560.6\ \omega - 2358$	0.99
	$E^{0'} = 364.6\ EA - 1859$	0.98
	$E^{0'} = 367.3\ \chi_R - 3268$	0.95
β-Diketones	$E_{pc} = -0.623\ E_{LUMO} - 3.607$	0.99
	$E_{pc} = 0.9415\ \omega - 3.176$	0.94
	$E_{pc} = 0.6169\ EA - 2.393$	0.84
Ferrocene-β-diketones:	$E^{0'} = -240\ E_{HOMO} - 1146$	0.92
	$E^{0'} = 98\ IP - 401$	0.87
	$E^{0'} = 2348\ \chi_R - 77$	0.76
Rh complexes	$E_{pa} = -0.339\ E_{HOMO} - 1.257$	0.94
	$E^{0'} = -0.351\ E_{HOMO-1} - 1.264$	0.98

the ferrocenyl moiety, gave an even better correlation of 0.98.

Linear equations derived for specifically related groups of compounds may therefore be used to theoretically estimate redox potentials to a large degree of accuracy.

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