A Frontier orbital energy approach to redox potentials

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Abstract. The prediction of the oxidation and reduction potentials of molecules is important in many research areas. A review of relationships obtained between frontier orbital energies (eV), the calculated ionization potentials (IP in eV), or adiabatic electron affinities (EA in eV) with the experimental oxidation and reduction potentials is presented, for selected series of β-diketones, rhodium-β-diketonato complexes, as well as metal-tris-β-diketonato complexes, with the metal Fe or Mn. The good linear relationships obtained for related series of complexes show that the oxidation and reduction potentials of these complexes can be predicted by their DFT-calculated energies.

1. Introduction

The Koopmans’ theorem, related to closed-shell Hartree–Fock theory, states that the first (vertical) ionization energy of a molecular system is equal to the negative of the Hartree–Fock orbital energy of the highest occupied molecular orbital (HOMO).\(^1\) Although the original Koopmans’ paper did not refer to the calculation of electron affinities as the energy of the lowest unoccupied molecular orbitals (LUMO), the theorem was extended to calculate electron affinities from LUMO energies.\(^2,3\) The theorem was also extended to the Kohn-Sham orbital energies of density functional theory (DFT) calculations.\(^4,5\) The energy involved in the oxidation (loss of electrons) or reduction (gain of electrons) of a complex, is closely related to the ionization energy (amount of energy required to remove an electron from the HOMO of a molecule in the gaseous state) and electron affinity (amount of energy released when an electron is added to the LUMO of a neutral molecule in the gaseous state) of the complex. In fact, the following approximate linear relationship between HOMO and LUMO energies and oxidation/reduction potentials can be deduced from the Marcus quadratic relationship for interfacial electron transfer: \(^6\)

\[
EO_{\text{OX/RED}} = a + b \cdot E_{\text{HOMO/LUMO}}; \quad \text{where } E_{\text{OX/RED}} \text{ are the experimental redox potentials; } E_{\text{HOMO/LUMO}} \text{ the calculated HOMO and LUMO energies; and } a \text{ and } b \text{ are constants.}
\]

We therefore here present a summary of empirical comparisons found between DFT calculated HOMO and LUMO energies and experimental oxidation and reduction values, obtained for the β-diketones and metal-β-diketonato complexes in Figure 1.

2. Discussion

Coordination of the enolated anion, \((\text{RCOCHCOR'})^-\) (Figure 1 (a)) of a β-diketone to a metal, produces a pseudo-aromatic ring with the metal. The electron donating properties of the R and R’ groups on the β-diketonato ligand, will thus change the electron density on the metal through the conjugation and thus the ease of oxidation and/or reduction of the metal. The energy of the frontier orbitals of β-diketones and metal-β-diketonato complexes will also be determined by the electron
donating properties of the R and R’ groups. By choosing the R and R’ groups to range from electron donating (like ferrocenyl, Fc) to electron withdrawing (like CF3), the abovementioned relationships are obtained over a large HOMO/LUMO energy and oxidation/reduction potential range. The order of electronegativity of the different R and R’ groups is as follows, from most to least electron withdrawing: PhNO2 > CF3 > CCl3 > CH3 > C4H3O > Ph > C4H3S > Fc.

The DFT calculated electronic energies of the neutral and oxidized/reduced complex with metal M were used to calculate the first ionization potential (IP) and the electron affinity (EA) values of the complexes:

\[
IP(M) = E(M) - E(M^+) \quad \text{and} \quad EA(M) = E(M^-) - E(M)
\]

2.1. β-diketones
The linear relations for the correlations found between the experimentally measured reduction potential of a series of β-diketones and their calculated LUMO energies and EA, are shown in Figure 2 and Figure 3 respectively. In the electro-active centre, the LUMO has π-character that is distributed mainly over the conjugated β-diketone backbone, allowing for the delocalization of the electron density, see Figure 4. The reduction potentials vary over more than 1 eV, indicating excellent electronic communication via conjugation between the electro-active centre and the substituent R groups. The DFT calculations showed that β-diketones containing electron withdrawing groups, have lower more negative LUMO energies, higher EA and are reduced at a higher, less negative potential.

β-diketones:

\[
E_{pc}(V \text{ vs. } Fc/Fc^+) = -0.63 \times ELUMO - 3.63 \quad R^2 = 0.99
\]

\[
E_{pc}(V \text{ vs. } Fc/Fc^+) = 0.62 \times EA - 2.39 \quad R^2 = 0.84
\]
The linear relations for oxidation of the metal (Fe) and their calculated HOMO energies and IP, in a series of ferrocenyl-containing β-diketones, are shown in Figure 6 and Figure 7, respectively. The HOMO is Fe-based, confirming the Fe oxidation, see Figure 5. The relationships obtained are:

Fc-containing β-diketones:

\[ E'(V \text{ vs. } \text{Fc/Fc}^+ ) = -0.24 \text{ E}_{\text{HOMO}} - 1.15 \quad R^2 = 0.92 \]

\[ E'(V \text{ vs. } \text{Fc/Fc}^+ ) = 0.10 \text{ IP} - 0.40 \quad R^2 = 0.86 \]

2.2. \( M(\beta\text{-diketonato})_3 \) complexes, \( M = \text{Fe or Mn} \)

Reduction of a complex involves the addition of an electron to the LUMO. The LUMOs of the octahedral \( M(\beta\text{-diketonato})_3 \) complexes with \( M = \text{Fe}^{III} \) or \( \text{Mn}^{III} \) are mainly metal based (Figure 8 and Figure 9), implying that the experimentally observed reduction during a cyclic voltammetry experiment, involve the reduction of the \( M^{III} \) to \( M^{II} \). The influence of the electron donating/withdrawing power of the \( R \) and \( R' \) groups of the coordinated \( \beta\text{-diketonato} \) complex on the metal reduction, is evident from the large experimental potential range. The relationship between the experimentally measured reduction potential and the calculated LUMO...
energies (Figure 10 and Figure 11) gave a better fit than the relationship between the experimentally measured reduction potential and the calculated EA (graphs not shown):

Fe(β-diketonato):  
\[ E^0' \text{ (V vs SCE)} = -0.59 \text{ ELUMO} - 2.74 \]  \[ R^2 = 0.96 \]
\[ E^0' \text{ (V vs SCE)} = 0.71 \text{ EA} - 1.94 \]  \[ R^2 = 0.94 \]

Mn(β-diketonato):  
\[ \frac{(E_{pc} + E_{pa})}{2} \text{ vs SCE/V} = -0.76 \text{ ELUMO} - 2.75 \]  \[ R^2 = 0.98 \]
\[ \frac{(E_{pc} + E_{pa})}{2} \text{ vs SCE/V} = 0.83 \text{ EA} - 1.95 \]  \[ R^2 = 0.91 \]

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2.3. Rh(β-diketonato)(L,L') complexes: \(^{11}\) \((L,L') = (P(OPh)_3,P(OPh)_3); (cod) or (CO),(PPh)_3)
Rh(β-diketonato)(L,L') complexes are experimentally oxidized to RhIII(β-diketonato)(L,L') in an irreversible two electron transfer process. The HOMO of the d6 RhI(β-diketonato)(L,L') complexes is mainly $d_{z^2}$ based (Figure 12). For the ferrocenyl-β-diketonato containing Rh(β-diketonato)(cod) complexes, the RhI to RhIII oxidation, is followed by oxidation of the ferrocenyl group (FeII to FeIII) at a slightly more positive potential. From the relationships presented in Figure 13 and given below we observe, as expected, that the higher the energy of the HOMO, the easier it is to remove the electrons during the oxidation process.

$$\begin{align*}
E_{pa} (\text{Rh in V vs. } \text{Fc/Fc}^+) &= -1.50 E_{HOMO} - 7.81 \quad R^2 = 0.85 \\
E_{pa} (\text{Rh in V vs. } \text{Fc/Fc}^+) &= -0.45 E_{HOMO} - 2.11 \quad R^2 = 0.89 \\
E_{pa} (\text{Rh in V vs. } \text{Fc/Fc}^+) &= 0.29 \text{IP} - 3.65 \quad R^2 = 0.97 \\
E_{pa} (\text{Rh in V vs. } \text{Fc/Fc}^+) &= -0.35 E_{HOMO} - 1.31 \quad R^2 = 0.90 \\
E_{pa} (\text{Fc in V vs. } \text{Fc/Fc}^+) &= -0.39 E_{HOMO-1} - 1.52 \quad R^2 = 0.99
\end{align*}$$

3. Conclusion
We have illustrated that for a series of complexes with similar structures, a linear relationship exists between the molecular orbital energies and their reduction and oxidation potentials obtained from cyclic voltammetry. These linear correlations can be used to estimate the redox potentials of unknown complexes, using the calculated HOMO and LUMO energy levels.

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