Computational chemistry insights in the REDOX Behaviour of Cr and W Fischer carbene complexes

Marile Landman, Jeanet Conradie and Petrus H. van Rooyen

1 Department of Chemistry, University of Pretoria, Private Bag X20, Hatfield, 0028, Republic of South Africa
2 Department of Chemistry, University of the Free State, 9300 Bloemfontein, Republic of South Africa.

phvr@up.ac.za

Abstract. An electrochemical study of a series of Fischer carbene complexes containing a heteroaryl group showed that Cr and W carbenes exhibit different electrochemical behaviour. The Cr carbenes are oxidized in two one electron oxidation processes, namely Cr(0) to Cr(I) and Cr(I) to Cr(II). On the contrary, Fischer carbene complexes of tungsten are directly oxidized from W(0) to W(II). The first reduction process observed for both W- and Cr-carbenes, is a one electron process. A density functional theory (DFT) computational chemistry study of the electronic structure of the Cr- and W-carbenes, showed that the oxidation is metal based and the reduction is located on the carbene ligand. The DFT calculations further showed that the Cr(II) species is a triplet and the W(II) species a closed shell singlet. The DFT calculated energies of the HOMO and LUMO of the neutral carbenes relate linearly to the experimental oxidation and reduction potential, respectively. These mathematical relationships obtained can be used to predict experimentally measured potentials of related Fischer carbene complexes.

1. Introduction

A transition metal carbene complex is an organometallic compound having a metal-carbon double bond, often denoted by M=CR₂. The first example of such a complex was synthesized by Fischer and Maasbol in 1964, (CO)₅W=C(Ph)(OCH₃) with the metal is in the 0 oxidation state [1]. Figure 1 shows how the structure of a typical Fischer carbene complex can be modified. For example, the carbene centre may be attacked by nucleophiles such as amines leading to the formation of aminocarbene complexes with liberation of alcohols. Hydrogens found on the α-carbon to the carbene are readily removed by a base, allowing the complex to be available for further reactions. Electrophiles, such as Lewis acids, may also coordinate to the heteroatom substituent through its lone pairs. Lastly, the ligand sphere of the metal may be altered in substitution reactions by replacing the carbonyl ligands with e.g. phosphines. The influence of the modifications on the electron density of the metal can theoretically be calculated utilizing computational chemistry techniques, and can experimentally be measured by cyclic voltammetry.

A cyclic voltammetry (CV) experiment [2] involves the application of linear potential scans to a stationary working electrode immersed in a solution containing the redox active species under investigation (analyte) while measuring the resulting current. The potential is scanned from a potential $E_i$ where no redox reaction takes place, to a potential where electron transfer is rapid as observed by an increasing current, till the current decays after the solution surrounding the working electrode is
depleted of the analyte and then the potential is reversed and scanned back to $E_1$. When the material has oxidations (or reductions) in the experimental potential range possible for the solvent, an anodic (or cathodic) wave will appear on the positive forward (or negative backward) scan, and a corresponding cathodic (or anodic) wave will be detected on the reverse scan if the oxidized (reduced) analyte is stable in the timescale of the CV experiment. If the two oxidation states (Ox/Red) are stable in the time scale of the experiment, the maximum (peak) currents in these two coupled waves should be approximately the same and the redox process is called chemically reversible. If the redox couples exhibiting fast electron transfer and the two oxidation states are stable in the time scale of the experiment, the potential difference ($\Delta E_p$) between the cathodic ($E_{pc}$) and anodic ($E_{pa}$) peaks potentials will be $\Delta E_p = E_{pc} - E_{pa} \approx (0.057 \, V/ \, n)$ ($n$ is the number of electrons transferred in the process) and the redox process is called electrochemically reversible. The potential midway between the two peak potentials is called formal electrode potential $E^0 = (E_{pc} - E_{pa})/2$ [3]. A slow exchange of redox species with the working electrode may lead to large peaks separations and the redox process is then considered electrochemical quasi-reversible (0.090 V $< \Delta E_p < 0.150$ V) or electrochemical irreversible ($\Delta E_p > 0.150$ V) [4]. A chemical irreversible system is one where only oxidation (or only reduction) is observed [5].

From a theoretical point of view, oxidation of the analyte in solution is the movement of an electron from the highest occupied molecular orbital (HOMO) of the analyte into the metal electrode and reduction is when the cell potential is sufficient to promote an electron into the lowest unoccupied molecular orbital (LUMO) of the analyte. The character of the HOMO (LUMO) of the analyte will thus tell where the oxidation (reduction) takes place. In addition, the ease of oxidation (reduction) should be related to the energy of the HOMO (LUMO). In fact, in many cases good linear relationships have been obtained between redox potentials and MO energy levels [6-8].

2. Discussion

2.1. Redox results
Fischer carbenes (Figure 1) have two electro-active centres, the metal centre and the carbene carbon [4],[9]. During cyclic voltammetry experiments of Fischer carbenes, generally one or more oxidation processes and one reduction process are observed; see Figure 2 [9] and Figure 3 [4]. The Cr carbenes are oxidized in two 1 e$^-$/oxidation processes, namely Cr(0) to Cr(I) and Cr(I) to Cr(II). On the contrary, Fischer carbene complexes of tungsten are oxidized in two 2 e$^-$/oxidation processes, namely from W(0) to W(II) and W(II) to W(IV). The first reduction process observed for both W- and Cr-carbenes, is a one electron process.
2.2. Computational chemistry DFT results

The metal-d character of the HOMO and HOMO-1 of the density functional theory (DFT) optimized neutral carbene confirms the metal oxidation, while the LUMO clearly shows that during reduction the carbene carbon is reduced to form a carbene-radical with the added electron density found to be distributed over the carbene ligand. The delocalization of the added electron over the carbene ligand can also be visualized by the Mulliken spin density plot of the reduced carbene. The DFT calculations further showed that the oxidized Cr(II) species is a triplet [9] while the W(II) species a closed shell singlet [4].

Substitution of one of the CO groups in the penta-carbonyl [(CO)$_5$W=C(OEt)(Th)] (L in Figure 1) with PPh$_3$, leads to tetra-carbonyl [(CO)$_4$(PPh$_3$)W=C(OEt)(Th)] with the PPh$_3$ group coordinated in a cis position or a trans position relative to carbene ligand C(OEt)(Th). Experimentally, trans-[(CO)$_4$(PPh$_3$)W=C(OEt)(Th)] is more easily oxidized at a lower potential (0.100 V lower) than the corresponding cis complex, see Figure 5(a). This is consistent with DFT calculations showing the trans complex to be more than 0.1 eV less stable than the corresponding cis complex, and that the calculated HOMO energy of the trans complex is 0.2 eV higher than that of the corresponding cis complex, implying that an electron will be more easily removed from the higher energy trans HOMO than from the cis HOMO. Experimentally it is found that the trans complexes isomerize to the more stable cis complexes, explaining the shoulder on the oxidation peak on the CV of trans-[(CO)$_4$(PPh$_3$)W=C(OEt)(Th)], while the CV of the more stable cis-[(CO)$_4$(PPh$_3$)W=C(OEt)(Th)]

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Figure 2. Cyclic voltammogram (CV) and linear sweep voltammogram (LSV) of c.a. 0.0005 mol dm$^{-3}$ solutions of [Cr(CO)$_5$(C(OEt)Th)] in CH$_3$CN / 0.1 mol dm$^{-3}$ [N$^\text{(Bu$_4$)}$]N][PF$_6$] on a glassy carbon-working electrode at a scan rate of 0.100 V s$^{-1}$. Data from reference 9.

Figure 3. Cyclic voltammogram (CV) and linear sweep voltammogram (LSV) of c.a. 0.0005 mol dm$^{-3}$ solutions of [W(CO)$_4$(PPh$_3$)(C(OEt)Th)] cis in CH$_3$CN / 0.1 mol dm$^{-3}$ [N$^\text{(Bu$_4$)}$]N][PF$_6$] on a glassy carbon-working electrode at a scan rate of 0.100 V s$^{-1}$. Data from reference 4.
exhibits only one sharp oxidation peak corresponding to the oxidation of cis-
 [(CO)₅(PPh₃)W=C(OEt)(Th)].

Figure 4. Selected frontier orbitals of the B3LYP/6-311G(d,p)/def2-TZVPP optimized structures of the neutral
 [M(CO)₅{C(OEt)Th}] complexes. The spin density plot of the
 optimized reduced radical anion (q = -1, S = ½) is also shown.
 (a) M = Cr and (b) M = W. Colour code of atoms (online
 version): C (black), H (white), O (red), S (yellow), W
 (turquoise), Cr (blue).

Figure 5. Cyclic voltammogram of the oxidation of c.a. 0.0005
 mol dm⁻³ solutions of (a) [W(CO)₄(PPh₃){C(OEt)Th}] cis and
 trans and (b) [Cr(CO)₅(dppe){C(OEt)Th}] mer and fac in
 CH₃CN / 0.1 mol dm⁻³ [¹(Bu₄)N][PF₆] on a glassy carbon-
 working electrode at a scan rate of 0.100 V s⁻¹.

Substitution of two of the CO groups in the penta-carbonyl [(CO)₅Cr=C(OEt)(Th)] (L and L’ in
 Figure 1) with 1,2-bis(diphenylphosphinoethane) (dppe), leads to tri-carbonyl
 [(CO)₄(dppe)Cr=C(OEt)(Th)] with the dppe group coordinated in a fac or mer position relative to the
carbene ligand C(OEt)(Th). DFT results on the relative energies of the fac and mer isomers indicated
that the mer isomers are considerably more stable than the fac isomers, in agreement with the fact that
the mer isomer is the main isomer observed experimentally. DFT calculations further showed that the
energy of the HOMO of the fac isomer was lower (more negative), than that of the mer isomer. More
energy will thus be needed to remove an electron from the more stable fac HOMO, implying that fac
will be oxidized at a higher potential. This results agrees with experimental observation when
comparing the CV of a pure \textit{mer} complex with that of a \textit{fac-mer} mixture, see Figure 5(b). DFT calculations also show that the oxidized \textit{mer}-cation is at least 0.3 eV more stable than the \textit{fac}-cation. Applying these energies to the Boltzmann distribution, results show the dominance of more than 99.9 \% \textit{mer}$. Thus after oxidation \textit{fac}$ will convert to \textit{mer}$$. This is also consistent with experimental observations that only one reduction peak coupled to the \textit{mer} and \textit{fac} oxidation peaks is observed on the CV that is ascribed to the reduction of the \textit{mer}$ cation [10].

2.3. Relationships
The close relationship between the energy of the frontier orbitals and the ease of removing (reduction) or adding (oxidation) an electron to it, is illustrated in the linear relationships obtained in Figure 6 for a series of Cr and W Fischer carbenes. These relationships can be utilized to design similar Cr or W Fischer carbenes with a specific stability towards oxidation and reduction.

![Figure 6](image_url)

Figure 6. Linear relationships between the DFT calculated $E_{\text{HOMO}}$ or $E_{\text{LUMO}}$ and the experimental oxidation $E_{\text{pa}}$ or reduction $E_{\text{pc}}$ potential of a series of Cr and W Fischer carbenes. Data obtained from reference 4, 9, 10, 11.

3. Conclusion
DFT can be considered a very useful technique to investigate and understand experimental observations by calculation of molecular properties which are difficult to measure experimentally. Here we illustrated how DFT calculations can be used to understand the oxidation and reduction center of Cr and W Fischer carbenes, to predict the relative stability of \textit{cis} and \textit{trans} or \textit{fac} and \textit{mer} isomers, and to obtain linear relationships between experimental redox values and DFT calculated energies.

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