Inorganica Chimica Acta 424 (2015) 316–321

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

# From gas-phase ionization energies to solution oxidation potentials: Dimolybdenum tetraformamidinate paddlewheel complexes

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ARTICLE INFO

*Article history:*
Received 16 July 2014
Received in revised form 17 September 2014
Accepted 18 September 2014
Available online 8 October 2014

*Keywords:*
Metal–metal bonds
Photoelectron spectroscopy
Cyclic voltammetry
Density functional theory
LFER
Substituent effects

ABSTRACT

The gas-phase ionization energies of a series of $Mo_2(DPhF)_4$ paddlewheel complexes (DPhF is the *N,N′*-diphenylformamidinate anion with *p*-$CH_3$, *p*-Cl, *m*-Cl, *p*-$CF_3$, or *m*-$CF_3$ phenyl substituents) have been measured by ultraviolet photoelectron spectroscopy (UPS) and compared with the solution oxidation potentials measured by cyclic voltammetry (CV) reported by Ren and coworkers. A linear relationship was found between the gas-phase ionization energies and the solution oxidation potentials. Density functional theory (DFT) computations clarify the individual electronic and thermodynamic factors that contribute to the correlation. The metal–metal delta bond electron energy is the largest factor in determining the solution oxidation potential. The substituents shift the metal–metal orbital energies by changing the through-space field potential at the metals rather than by an inductive change in charge at the metals or orbital overlap effects. The cation solvation energies determine the extent that the potential shifts are attenuated in solution. The results show that substituent field effects and solvation have major roles in determining the dimetal redox chemistry even when the dimetal unit is protected from direct interaction with the substituent and the solvent.



## 1. Introduction

Dimetal paddlewheel complexes [1] have an extraordinarily wide range of electron energies and electrochemical potentials for a single class of molecules. For example, among the dimolybdenum paddlewheel complexes alone, the first ionization energies span a range of over 4 eV ($Mo_2(O_2CCF_3)_4$, 8.63 eV [2]; $Mo_2(TEhpp)_4$, 4.27 eV [3]). The analogous $W_2(TEhpp)_4$ complex, where TEhpp is a tetraethyl bicyclic guanidinate ligand, has the lowest ionization energy of any chemical reducing agents at 3.45 eV [4]. These electron energies are precisely measured in the gas phase and accurately referenced to the vacuum level of an electron at zero kinetic energy by gas-phase ultraviolet photoelectron spectroscopy (UPS) [5]. As such, these experimental energies provide a precise benchmark for quantum chemical computations. To what extent can the detailed understanding of electron energies in the gas phase extend to understanding chemical behavior in solution? Numerous investigators have noted a correlation between gas-phase ionization energies measured by UPS and solution oxidation potentials measured electrochemically [6–12]. Most often solution oxidation potentials are less sensitive to chemical substitution than gas-phase ionization energies, with a ratio of about 0.7 found for a variety of compounds [7,10–12]. Recently we have found a case where the oxidation potentials are more sensitive than the ionization energies [13]. Knowledge of the factors that relate the electron potentials in the gas phase to those in solution contributes to understanding the chemical behavior, either directly in the case of oxidative reactions or indirectly through thermodynamic reaction cycles.

Among the paddlewheel complexes, molecules of the type $M_2(DPhF)_4$ (where DPhF is the common notation for the *N,N′*-diphenylformamidinate ligand, see Chart 1) have been prepared with more metals than any other ligand set. Complexes with these diphenylformamidinate ligands have been investigated for many applications, ranging from anti-cancer applications in biology to carbene activation in catalysis to light emitting diode research in material science [14,15]. The diphenylformamidinate ligands are convenient for the present study of electronic effects because the phenyl rings can be substituted with electron-withdrawing or electron-donating groups simply by changing the aniline in the synthetic procedure. The compounds in Chart 1 are numbered in the

*Abbreviations:* UPS, ultraviolet photoelectron spectroscopy; CV, cyclic voltammetry; DFT, density functional theory; DPhF, the anion of *N,N′*-diphenylformamidinate; TEhpp, the anion of 3,3,9,9-tetramethyl-1,5,7-triazabicyclo [4.4.0] dec-4-ene; VIE, vertical ionization energy; AIE, adiabatic ionization energy.

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http://dx.doi.org/10.1016/j.ica.2014.09.021
0020-1693/

order of increasing Hammett σ parameter [16]. The foundation for the present study has been established by Ren and coworkers, who found a linear free energy relationship between the oxidation potentials and Hammett substitution constants (σ) with a reaction constant ρ of 85 mV [17,18].

Both photoelectron spectroscopy and electrochemistry measure the effects of ligand substitution on electron energies, but the two methods of electron removal differ in several ways. Photoelectron spectroscopy is a measure of the *spectroscopic energy* in the gas phase on a fast timescale, whereas cyclic voltammetry is a measure of the *thermodynamic potential* in solution, subject to the kinetics of the process. These paddlewheel complexes are attractive for the present study because the oxidations are chemically reversible and electrochemically quasi-reversible, so kinetic effects on the measure of $E_{1/2}$ are not appreciable. In addition, because there is little change in geometry with oxidation for these molecules, the solvent cavities, and vibrational, translational, and rotational contributions to the Gibbs energies are similar in the neutral and cation species and contribute little to the oxidation potential. These contributions are discussed in detail in Section 3.4.

Consequently, these molecules are ideal systems to study the relation between ionization energies and oxidation potentials. It is found that the substitutions on the phenyl rings cause substantial shifts in the gas-phase ionization energies. Similar to the oxidation potentials, the ionization energies are found to correlate with the Hammett parameters of the substituents. Interestingly, the different donor abilities of the substituents do *not* alter the electron density on the metals, but instead perturb the potential field at the metals via a change in the local charge distribution (local dipoles) of the phenyl groups. The change in local dipoles of the phenyl groups also has an effect on the solvation energies. The slope of the trend in oxidation potentials vs. ionization energies is determined by the extent that the solvation energies and ionization energies are influenced by the change in dipole moments of the phenyl groups. The shifts in oxidation potentials of the metal–metal δ bonds caused by the substituents can occur without explicit inductive, orbital overlap, or solvent interactions directly with the metals.

## 2. Methods

### 2.1. Ultraviolet photoelectron spectroscopy (UPS)

The $Mo_2(DPhF)_4$ compounds were prepared according to published procedures [17,19]. The gas-phase photoelectron spectra were recorded using an instrument that features a 360 mm radius, 80 mm gap hemispherical analyzer [20], and custom-designed excitation source, sample cells, detection and control electronics, and methods that have been described in detail previously [21], The temperature was monitored using a "K"-type thermocouple attached directly to the sample cell. Sublimation temperatures (°C) for collection of the spectra of these substituted $Mo_2(DPhF)_4$ systems were: **1** (*p*-$CH_3$) 240°,**2** (H) 220°, **3** (*p*-Cl) 310°, **4** (*m*-Cl) 310°, **5** (*m*-$CF_3$) 210°, and **6** (*p*-$CF_3$) 220°. All samples sublimed cleanly without evidence of contamination or decomposition in the spectra.

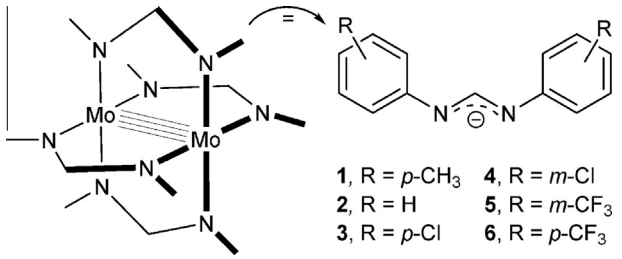


**Chart 1.** Paddlewheel structure of the dimolybdenum complexes and the substituted diphenylformamidinate ligands in this study.

The argon $^2P_{3/2}$ ionization at 15.759 eV was used as an internal calibration lock of the absolute ionization energy. The difference between the argon $^2P_{3/2}$ and the methyl iodide $^2E_{1/2}$ ionization at 9.538 eV was used to calibrate the ionization energy scale. During data collection the instrument resolution, measured using the full width at half-maximum of the argon $^2P_{3/2}$ ionization, was 0.020–0.030 eV. All data are intensity corrected with an experimentally determined instrument analyzer sensitivity function that assumes a linear dependence of analyzer transmission (intensity) to the kinetic energy of the electrons within the energy range of these experiments. Reported vertical ionization energies have an experimental uncertainty of ±0.02 e V.

The ionization bands in the photoelectron spectra are represented analytically with asymmetric Gaussian peaks [22]. The minimum number of peaks was used to represent the contours of the data. The experimental variance of the photoelectron data are represented in Fig. 1 by the vertical length of each data mark [21]. A more detailed discussion of the analytical representation of the data has been presented elsewhere [21].

### 2.2. Computational model

All computations were carried out with the Amsterdam Density Functional program version adf2013.01 [23–25]. Several density functional and basis set models were recently tested for their ability to account for the geometric structures and first gas-phase ionization energies of quadruple-bonded ditungsten paddlewheel complexes [4]. Seventy-five functionals were tested at the level of the local density approximation (LDA), the generalized gradient

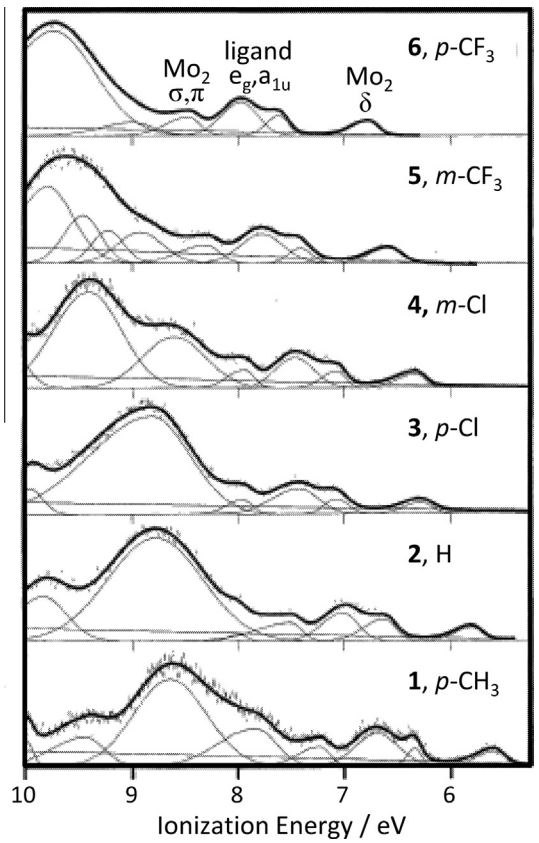


**Fig. 1.** He I photoelectron spectra.