

Computational study of substituent effect on the electronic properties of ferrocylidene acetophenones complexes

Maryam Rahimi^a, Saeid Jamehbozorgi^{b,*}, Henry Chermette^c, Reza Ghiasi^d, Mahboubeh Poor Kalhor^e

^aDepartment of chemistry, faculty of science, Arak branch, Islamic Azad University, P.O. BOX 38361-1-9131, Arak, Iran

^bDepartment of chemistry, Faculty of science, Hamedan Branch, Islamic Azad University, P.O. BOX 65181-15743, Hamedan, Iran

^cInstitut des sciences analytiques, Université Claude Bernard LYON-1, Lyon, CNRS UMR 5280, 43 boul. du 11 Nov. 1918, 69622 Villeurbanne, France

^dDepartment of Chemistry, Faculty of science, East Tehran Branch, Islamic Azad University, P.O. BOX 16511-53311, Tehran, IRAN

^eDepartment of Chemistry, faculty of Science, Farhangian University, Tehran, Iran

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Abstract

In this study, the substituent effect on the electronic, spectroscopic properties and thermodynamic parameters of neutral and oxidized states of ferrocylidene acetophenone complexes is investigated by adopting the hybrid meta exchange-correlation functional of M06-2X. The frontier orbitals and the highest occupied molecular orbitals–lowest unoccupied molecular orbitals gaps of the substituted compounds are determined. Ionization potential (IP), electron affinity, and reorganization energy values of these molecules are estimated. The thermodynamic parameters (free energy and enthalpy) of the oxidation reaction of the studied complexes are calculated. Also, a variation on the wavenumber of carbonyl group in both states is revealed as the correlations between the evaluated properties and Hammett's constant are explored.

Keywords: Ferrocene; substituent effect; ionization potential; electron affinity; thermodynamic parameters.

Introduction

Ferrocene and its derivatives are well-known redox active materials and have been extensively used to fabricate modified electrodes for electrochemical sensors and biosensors. Substituting the functional groups of ferrocene offers the prospect of controlling its properties, such as its solubility,

stability, oxidation potential, and reversibility of oxidation wave (important for its role as an electron transfer mediator). Adjusting the outlined molecular properties is essential for biosensor applications. In this respect, different ferrocene derivatives have been developed. In this sense, the electrochemistry of some

*Corresponding author: Saeid Jamehbozorgi

ferrocene derivatives have been studied, and the redox potential and substituent effects have been reported [1].

As the most straightforward method of the adjusting ferrocene properties is substitution, many studies have reported the effect of different substituents on the chemical and physical characteristics of ferrocene. Such studies can be facilitated by quantum chemical (QC) evaluations since they are useful in relating structural changes to electronic properties [2-7]. That is why various computational investigations have reported the impact of substituting diverse functional groups on the structural, spectroscopic, and electronic features of organometallic complexes [8-20]. Furthermore, quantum chemistry can provide quantitative scales of the substituent parameters to clarify the steric or polar effects of the utilized substituents on different molecular properties. For example, the Hammett constant (σ_p) [21] can describe the electronic effects of the substituted functional groups on the equilibrium and rate constants of a reacting molecule. In this investigation, we studied the substituent effect on the electronic properties and thermodynamic parameters of the

neutral and oxidized states of ferrocylidene acetophenone complexes using the M06-2X method.

Computational methods

The QC calculations were performed using the Gaussian 09 program [22]. While the main group elements of the compounds were described by the standard basis set of 6-311G(d,p), the Fe element was considered using the standard Def2-TZVPPD basis set [23]. The geometries of the compounds were optimized by the hybrid functional of M062X, as developed by Truhlar and Zhao [24]. This method is hybrid meta exchange-correlation functionals. The M06-2X functional is a high-nonlocality functional with double the amount of nonlocal exchange (2X). Substituents are F, Cl, and CN, and EDG substituents are OH and Me. Table 1 shows the absolute energy of the neutral and oxidized states of these complexes. Illustration of the substituent effect on the electronic properties in this study has been reported. EWG Adiabatic ionization potential (IP(a)), an optimized structure for both the neutral and charged molecule) and vertical IP(v), (at the geometry of the neutral molecule) values were calculated for these molecules.

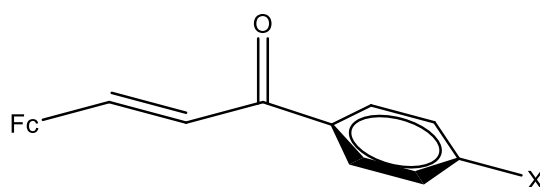


Figure 1. The structure of ferrocylidene acetophenones complexes (X=substituent)

Ionization potential

Figure 1 displays the structures of the studied ferrocene derivatives. We selected electron-withdrawing groups

(EWG) and electron-donating groups (EDG) for The IP(a) and IP(v) values, which were larger for molecules containing EWGs than for those having

EDGs (Table 1). A good linear correlation was seen between the IP values and the σ_p Hammett constants (Figure 2):

$$IP(a) = 0.2325\sigma_p + 7.3036; R^2 = 0.9612$$

$$IP(v) = 0.2349\sigma_p + 7.3487; R^2 = 0.9542$$

Electron affinity

Adiabatic and vertical electron affinity values of the studied ferrocene

derivatives have been summarized in Table 1. It can be seen that the EA(a) and EA(v) values are smaller for molecules containing EWGs than for those having EDGs. A good linear correlation is seen between the EA values and the σ_p Hammett constants:

$$EA(a) = -0.6462\sigma_p - 0.8788; R^2 = 0.9347$$

$$EA(v) = -0.6950\sigma_p - 0.6234; R^2 = 0.9343$$

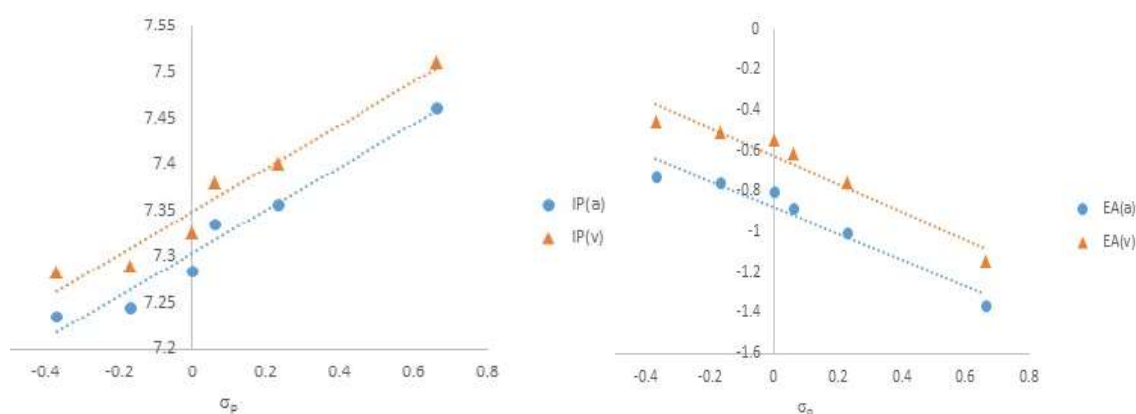


Figure 2. Dependencies of vertical, adiabatic ionization potential (IP), vertical and adiabatic electron affinity (EA) values on the Hammett's constant in the ferrocylidene acetophenones complexes

Table 1. Adiabatic ionization potential (IP(a), eV), vertical ionization potential (IP(v), eV), Adiabatic electron affinity (EA(a), eV) and vertical electron affinity (EA(v), eV) values of the studied ferrocylidene acetophenones. σ_p values are Hammett's constant

X	σ_p	IP(a)	IP(v)	EA(a)	EA(v)
OH	-0.37	7.24	7.28	-0.73	-0.45
Me	-0.17	7.25	7.29	-0.76	-0.51
H	0.00	7.28	7.33	-0.80	-0.54
F	0.06	7.33	7.38	-0.88	-0.62
Cl	0.23	7.36	7.40	-1.00	-0.76
CN	0.66	7.46	7.51	-1.36	-1.15

Electron reorganization energy ($\lambda_{\text{electron}}$)

The $\lambda_{\text{electron}}$ can be expressed as follows:

$$\lambda_{\text{electron}} = \text{EEP} - \text{EA}(v)$$

EEP (electron extraction potential) is the energy difference from E to E⁻ (anionic), using E⁻ geometric structure in calculation [25,26]. It can be seen that the $\lambda_{\text{electron}}$ values are larger for molecules containing EWGs than for those having EDGs (Table 2).

Hole reorganization energy (λ_{hole})

λ_{hole} for hole transfer can be expressed as follows:

$$\lambda_{\text{hole}} = \text{IP}(v) - \text{HEP}$$

HEP (hole extraction potential) is the energy difference from E (neutral molecule) to E⁺ (cationic), using E⁺ geometric structure in calculation. It can be seen that the λ_{hole} values are larger for molecules containing EWGs than those having EDGs. The mobility of charges has been established to be related mainly to the internal reorganization energy $\lambda_{\text{hole/electron}}$.

The data in Table 2 show that the λ_{hole} values for all molecules are less than their corresponding $\lambda_{\text{electron}}$ values, which indicates the electron transfer rate is slower than the hole transfer rate.

Table 2. Electron Extraction potential (EEP, eV), hole Extraction potential (HEP, eV), Electron reorganization energy ($\lambda_{\text{electron}}$, eV) and Hole reorganization energy (λ_{hole} , eV) values of the studied ferrocylideneacetophenones

X	HEP	λ_{hole}	EEP	$\lambda_{\text{electron}}$
OH	7.19	0.09	1.04	1.49
Me	7.20	0.09	1.05	1.56
H	7.24	0.08	1.09	1.64
F	7.28	0.09	1.18	1.80
Cl	7.31	0.10	1.26	2.02
CN	7.42	0.09	1.58	2.73

Vibrational analysis

The wavenumber values of carbonyl stretching of the studied complexes for neutral and oxidized states are listed in Table 3. It can be found that these values increase in the presence of the EWGs. In contrast, $\nu(\text{CO})$ values decrease in the presence of EDGs. On the other hand, $\nu(\text{CO})$ values are higher in the oxidized than in the neutral state.

Thermodynamic parameters

The thermodynamic parameters of the oxidation of ferrocylidene

acetophenone complexes are shown in Table 4. It can be seen that the oxidation reaction is not spontaneous. On the other hand, ΔH values reveal that this reaction is endothermic. The dependencies of the thermodynamic parameters on the Hammett's constant were explored. The linear correlations were:

$$\Delta G = 7.903\sigma_p + 166.95; R^2 = 0.9064$$

$$\Delta H = 5.4719\sigma_p + 167.22; R^2 = 0.9619$$

It can be found that the thermodynamic parameters are higher in the presence of EWGs as compared to that in the presence of EDGs.

Analysis of molecular orbitals

The frontier orbital energy values and their gap of the studied complexes in the neutral and oxidized states are given in Table 5. It can be seen that in the

presence of X = EWGs, the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively) are more stable as compared to that in the presence of EDGs. It can be found that the HOMO–LUMO gap is reduced when X = EWGs.

Table 3. The wavenumber values (cm⁻¹) of carbonyl stretching of the studied ferrocylidene acetophenones

X	$\nu(\text{CO}), \text{neutral}$	$\nu(\text{CO}), \text{oxidized}$
OH	1790.3097	1795.4800
Me	1794.0735	1801.9298
H	1795.9526	1807.0277
F	1793.8530	1804.1256
Cl	1796.4697	1804.6933
CN	1800.3199	1813.0268

Table 4. Thermodynamic values (ΔG , ΔH) (kJ/mol) of the studied ferrocylidene acetophenones in the neutral and oxidized states

X	neutral		oxidized		ΔG	ΔH
	G	H	G	H		
OH	-2147.3576	-2147.2891	-2147.0951	-2147.0256	164.72	165.36
Me	-2111.4195	-2111.3497	-2111.1565	-2111.0857	165.02	165.62
H	-2072.1380	-2072.0719	-2071.8743	-2071.8049	165.48	167.53
F	-2171.3861	-2171.3181	-2171.1177	-2171.0505	168.41	167.94
Cl	-2531.7489	-2531.6796	-2531.4794	-2531.4113	169.09	168.35
CN	-2164.3794	-2164.3076	-2164.1050	-2164.0354	172.20	170.76

A study of linear correlation seen between the frontier orbital energy and the σ_p Hammett constants in the neutral state showed the following correlations:

$$E(\text{HOMO}) = -0.0331\sigma_p - 0.3883; R^2 = 0.7783$$

$$E(\text{LUMO}) = -0.0085\sigma_p - 0.2154; R^2 = 0.9632$$

Therefore, there is a good linear correlation between the $E(\text{LUMO})$ energy and the σ_p Hammett constants in the neutral states. On the other hand, oxidation results in an increase in the stability of frontier orbitals and a decrease of the HOMO-LUMO gap values. A good linear correlation was seen between the frontier orbital energy and the σ_p Hammett constants in the oxidized states:

$$E(\text{HOMO}) = -0.012\sigma_p - 0.2826; R^2 = 0.9705$$

$$E(\text{LUMO}) = -0.0271\sigma_p - 0.0435; R^2 = 0.9408$$

Figure 3 presents plots of frontier orbitals in the ferrocylidene acetophenone complex ($X = \text{H}$). It can be found that the ferrocene fragment has more contribution in HOMO than in LUMO.

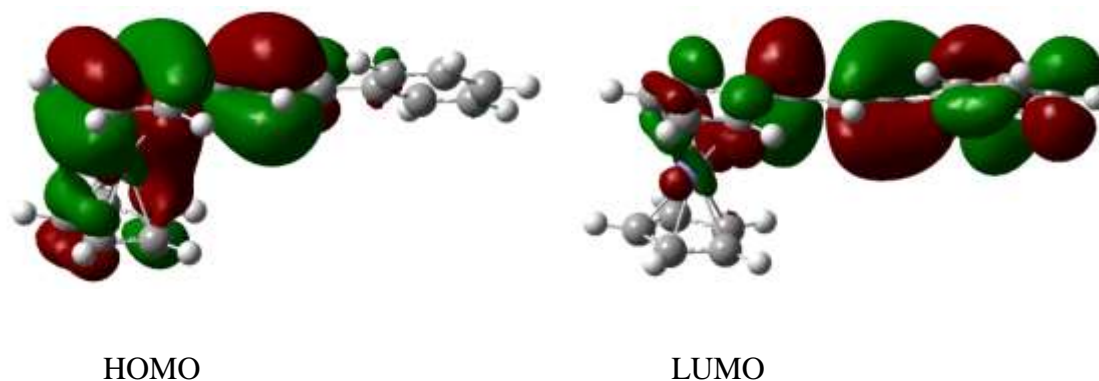


Figure 3. Plots of frontier orbitals in the ferrocylidene acetophenone complex ($X=\text{H}$)

Table 5. Frontier orbital energy (eV) and HOMO-LUMO gap (eV) values of the studied ferrocylidene acetophenones in the neutral and oxidized states

X	neutral			oxidized		
	$E(\text{HOMO})$	$E(\text{LUMO})$	Gap	$E(\text{HOMO})$	$E(\text{LUMO})$	Gap
OH	-7.59	-1.00	6.58	-10.06	-5.80	4.26
Me	-7.61	-1.05	6.56	-10.45	-5.81	4.64
H	-7.66	-1.11	6.55	-10.80	-5.85	4.95
F	-7.73	-1.18	6.55	-10.76	-5.88	4.88
Cl	-7.77	-1.31	6.46	-10.58	-5.90	4.68
CN	-7.90	-1.74	6.16	-11.13	-6.03	5.10

Conclusion

The computational study of substituent effect on the electronic properties of ferrocylidene acetophenone complexes showed that, $EA(a)$ and $EA(v)$ values are smaller for molecules containing EWGs than for those having EDGs. $IP(a)$ and $IP(v)$ values are larger for molecules containing EWGs than for those having EDGs. The λ_{hole} values for

all molecules are less than their corresponding $\lambda_{\text{electron}}$ values indicating that the electron-transfer rate is slower than the hole transfer rate. Oxidation results in increasing the stability of frontier orbitals and decreasing the HOMO-LUMO gap values. $\nu(\text{CO})$ values increase in the presence of the EWGs. In contrast, $\nu(\text{CO})$ values decrease in the presence of EDGs. On the other

hand, $\nu(\text{CO})$ values are higher in the oxidized state than in the neutral one. On the basis of the thermodynamic parameters, the oxidation reaction is not spontaneous but endothermic.

Acknowledgements

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