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THE DISSOCIATION ENERGIES OF METALLOCENES AND THEIR INFLUENCE ON INTERATOMIC DISTANCES

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Summary

The bond orders of the C—C bonds in metallocenes reflect the extent of π-bonding which in turn determines the strength of the metal—ligand bond. Using Pauling's bond distance—bond order relationship the bond orders of the C—C bonds and the number of π-electrons in the metal—ligand bonds are derived. The values are correlated with observed dissociation energies, allowing estimation of the energies of the highest occupied molecular orbitals, and the energies are used to predict the metal—ligand distances.

1. Introduction

The bond orders n of the C—C bonds in metallocenes are derived from observed C—C distance d_n according to Pauling's bond distance—bond order relation [1];

$$d_n = d_1 - (d_1 - d_2)\,\frac{1.84(n-1)}{0.84n + 0.16} \qquad (1)$$

where d_1 is the single bond distance (1.504 Å) and d_2 the double bond distance (1.334 Å). The number n_π of π-electrons transferred from the two cyclopentadienyl rings to the metal acceptor orbitals d_{xz}, d_{yz} [2] is given by the expression [3,4]:

$$n_\pi = 10(1.6 - n) \qquad (2)$$

where 1.6 is the bond order of the C—C bond in a free cyclopentadienyl anion. The mean dissociation energy is given by eq. 3, when the molecule is not des-

$$\bar{D} = 164\, n_\pi - 212 \text{ kJ} \qquad (3)$$

tabilized by occupation of the antibonding states.

The electron pairing energy is 60 B for the configuration $e_{2g}{}^4a_{1g}{}^2$ when B is

TABLE 1

THE LIGAND FIELD PARAMETERS AND PREDICTED M—C DISTANCES IN METALLOCENES

Metallocene MCp_2	D (kJ) observed	Observed distances (Å)		Used C—C distance (Å) (bond order) [a]	Ligand field parameters (kJ)		Bond order of M—C bond	Calculated M—C distance (Å)
		C—C	M—C		This work	Spectroscopic [5]		
$FeCp_2$	292.9 [10] (296.4)	1.431	2.058 [12]	1.431 (1.29) [0.6875] <1.2037>	Δ_1 74.2 B 4.92	81.0 4.92	0.5167	2.063
$RuCp_2$	368 [11] [b] (362)	1.439	2.196 [13]	1.439 (1.25) [0.6875] <1.3668>	Δ_1 100.5 B 2.73	— —	0.5833	2.195
$NiCp_2$	239.1 [10]	1.430	2.196 [14]	1.429 (2.302) [0.6875] <1.1855>	Δ_1 53.90 Δ_2 167.3	48.24 178.5 B 7.13	0.2883	2.197
VCp_2	351 [10] (351.34)	1.434	2.280 [15]	1.438 (1.2565) [0.6875] <1.3889>	Δ_1 46.33	45.83 B 5.31	0.4480	2.286
$MnCp_2$	(220.8)	1.429	2.383 [9]	1.427 (1.3125) [0.6875] <1.4864>	Δ_1 46.13 Δ_2 46.13 B 9.92	48.2	0.4482	2.383

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[a] The bond orders of the C—C bonds are given in parentheses and the single bond radii in brackets; [$r_C(1)$], <$r_M(1)$>. [b] The mean dissociation energy of ruthenocene is calculated from the heat of formation 288.7 kJ [11] according to the data and procedure given in ref. 10.

the Racah parameter. The nature of eq. 3 indicates that n_π cannot attain the maximum value of 4, so that the electron pairing energy can be derived according to the expression 4:

$$60\,B = 328(4 - n_\pi)\ \text{kJ} \tag{4}$$

In metallocenes with the configuration $e_{2g}{}^4a_{1g}{}^2(e^*_{1g})^n$ for $n = 1$ or 2, n_π calculated from the observed C—C distance does not give a correct value for D by use of eq. 3. Use of the observed mean dissociation energy will give a smaller value n'_π, which can be used in calculating the electron pairing energy by eq. 4. The destabilization energy $n\Delta_2$ of the antibonding electrons corresponds to $(4 - n_\pi)$ in n_π-energy units and; therefore the right hand side of eq. 4 gives $n\Delta_2$.

In vanadocene and the isoelectronic compounds the expression 5 affords the ligand field parameters Δ_1 [3];

$$n_\pi = 4 - (2\Delta_1/164) \tag{5}$$

Thus for the configuration $e_{2g}{}^2a_{1g}{}^1$ the energy change accompanying the variation of n_π by an electron is half (164 kJ) since the ligand field stabilization is $2\Delta_1$, half the full energy contribution of the e_{2g} states.

An alternative expression (6) for $\bar{D}$ was proposed;

$$2\bar{D} = 95.49\,n_\pi + 4\,\Delta_1 \tag{6}$$

for the $e_{2g}{}^4a_{ig}{}^2$ configuration [3]. The dissociation energy for the configuration $e_{2g}{}^4a_{ig}{}^2(e^*_{ig})^n$ is determined by use of n'_π derived from eq. 3. It is obvious that eq. 6 will give a value of Δ_1 twice the actual value for the $e_{2g}{}^2a_{ig}{}^1$ configuration.

The equations 1—7 permit calculation of the energies of the highest occupied molecular orbitals, and the nature of the relation between these energies and the dissociation energies of metallocenes. The order of the energies of those orbitals, $e_{2g} < a_{ig} < e^*_{ig}$, is established on the basis of absorption, ionization photoelectron spectra [5,6] and MO calculations [7].

The metal—ligand distances, like the dissociation energies, can be accounted for in terms of the energies of the highest occupied molecular orbitals. Short metal—ligand distances are associated with the $e_{2g}{}^4a_{ig}{}^2$ configuration, whereas the elongation of the metal—carbon distances characterize configurations with occupied anti-bonding states or an electron deficiency in the e_{2g} states. An illustrative examples is 1,1'-methylcyclopentadienylmanganese for which the Mn—C distances 2.14(2) Å and 2.42(1) Å, respectively, are observed in the low spin ${}^2E_{2g}$ and high spin ${}^6A_{ig}$ forms [8].

Table 1 gives calculated metal—carbon distances M—C using the ligand field parameters derived according to eq. 1—6. The metal—carbon distance d_n is calculated according to Pauling's logarithmic equation:

$$d_n = d_1 - 0.6 \log n \tag{7}$$

where d_1 is the sum of the single bond radii of the metal $r_M(1)$ and carbon $r_C(1)$ and n the bond number. The single bond radius of the divalent metal with the electron configuration nd^q is calculated according to Pauling's set of empirical equations:

$$r_M(1) = 1.825 - 0.043\,z - (1.6 - 0.100\,z)\delta \tag{8}$$

for $n = 3$ and

$$r_M(1) = 2.001 - 0.043\, z - (1.627 - 0.100\, z)\delta \tag{9}$$

for $n = 4$ and

$$r_M(1) = 1.850 - 0.03\, z - (1.276 - 0.070\, z)\delta \tag{10}$$

for $n = 5$; $z = q + n_\pi$

where z is the number of electrons in the valence shell of the metal atom and δ the d-character is derived from theoretical considerations.

The maximum d-character $\delta = 2/6$ is predicted for the metal in metallocenes with the $e_{2g}{}^4 a_{1g}{}^2$ configuration. The two metal acceptor orbitals d_{xz} and d_{yz} contribute 2/6 of the total number of orbitals used by the metal in bonding.

The single bond radius of carbon is derived from the observed C—C distance according to eq. 7 where in place of n we put $n' = n/_{1.6}$ [3].

2. The M—C distances

(i) In metallocenes with the $e_{2g}{}^4 a_{1g}{}^2$ configuration

The bond order of the M—C bond is $n_\pi/6$ and the M—C distance is determined by use of eq. 7.

(ii) In metallocenes with the $e_{2g}{}^4 a_{ig}(e^{\star}_{ig})^2$ configuration

The total destabilization is $60\,B + 2\,\Delta_2$, hence the bond order determining the M—C distance derived from eq. 7 is $n = \frac{1}{6}[4 - (60\,B + 2\,\Delta_2)/328]$. Alternatively $n = \frac{1}{6}(n'_\pi - 2\,\Delta_1/328)$.

(iii) In metallocenes with the $e_{2g}{}^2 e_{1g}{}^1$ configuration

The bond order of the M—C bond is $n = \frac{1}{6}(n_\pi/2 + 30\,B/_{164})$. For vanadocene the Racah parameter $B = 5.31$ kJ derived spectroscopically [5] is used. The d-character of the metal valence orbitals is adjusted by the use of the value of 1/6 for δ in eq. 8.

(iv) In metallocenes with the $e_{2g}{}^2 a_{ig}{}^1 (e^{\star}_{ig})^2$ configuration

The M—C distances is determined by the bond order $n = \frac{1}{6}[n_\pi/_2 + (30\,B - 2\,\Delta_2)/_{164}]$. The d-character of the metal valence orbitals is assumed to be zero i.e. $\delta = 0$, $\Delta_1 = \Delta_2$ corresponds to zero ligand field contribution. The ligand field parameters are given by;

$$2\,\Delta_1 + 2\,\Delta_2 = 164(4 - n_\pi) \tag{12}$$

The observed distances in manganocene are C—C 1.429 ± 0.005 Å Mn—C 2.383 ± 0.009 Å [9]. The number of π-electrons $n_\pi = 2.875$ is calculated for $n = 1.3125$ (eq. 1), $r_C(1) = 0.68755$ based on the C—C distance 1.427 Å. The ligand field parameters $\Delta_1 = \Delta_2 = 46.13$ kJ are obtained. The value $\Delta_1 = 48.2$ kJ has been estimated from the ionisation photoelectron spectrum of manganocene [5]. The observed Mn—C distance is used to derive the Racah parameter $B = 9.92$ kJ.

The mean dissociation energy of manganocene is obtained according to eq. 6

where n_π gives the bond order of the M—C bond $n_\pi/6$.
The mean dissociation energy of vanadocene is obtained in a similar manner.

The calculated dissociation energy of manganocene $\tilde{D}$ = 220.8 kJ is in good agreement with the value of 213 kJ reported by Russian authors [16].

3. Conclusion

The results are summarized in Table 1. The agreement of calculated ligand field parameters and values obtained from independent methods is quite satisfactory. The observed interatomic distances can be related to the nature of bonding. Since unoccupied antibonding orbitals do not contribute to the ground state of the molecule, it is not possible to derive energies of those orbitals. The elongation of the metal—ligand bond occurs in metallocenes with populated antibonding states. Similarly an electron deficiency in the bonding orbitals causes an elongation of the metal—ligand bond. The bond distances can be explained in terms of the electronic configuration and energies of the occupied molecular orbitals. The relation between the dissociation energies and energies of the highest occupied molecular orbitals is described elsewhere [3,4].

References

1 L. Pauling; The Nature of the Chemical Bond, Cornell University Press, Ithaca N.Y. 1960.
2 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Interscience, New York, 1972.
3 A.M. Mulokozi, Proceedings XXth International Conference Coordination Chemistry, December 1979, Calcutta, India.
4 A.M. Mulokozi, Conference Paper, IX-Intern. Conf. Organometal. Chem., 3—7 September, 1979, Dijon, France.
5 S.Evans, M.L.H. Green, B. Jewitt, G.A. King and F.A. Orchard; J. Chem. Soc. Faraday II, 70 (1974) 356.
6 R. Prins, J. Mol. Phys., 19 (1970) 603.
7 E.M. Suhtorovich and M.E. Dyatkina, J. Struct. Chem. U.S.S.R., 1 (1960) 98.
8 A. Almenningen, S. Samdal and A. Haaland, J. Chem. Commun., (1977) 14.
9 A. Almenningen, A. Haaland and T. Motzfeldt; Selected Topics Str. Chem. Univ. Oslo, Norway, (1967) 105.
10 G. Pilcher in Int. Rev. Sci. Phys. Chem. Series II, Vol. 10 Butterworths, London, 1975.
11 A.G. Turnbull, Austr. J. Chem., 20 (1967) 2059.
12 R.K. Bohm and A. Haaland, J. Organometal. Chem., 5 (1966) 470.
13 A. Haaland and J.E. Nielson, Acta Chim. Scand., 22 (1968) 2653.
14 L. Hedberg and K. Hedberg, J. Chem. Phys., 53 (1970) 1228.
15 E. Gard, A. Haaland, D.P. Novak and R. Seip, J. Organometal. Chem., 88 (1975) 181.
16 V.I. Tel'noi and I.B. Rabinovich, Russ. Chem. Rev., 46 (1977) 687.