PRELIMINARY NOTES

Ligand field absorption bands and *d* orbital splitting in ferrocene*

The nature of the bonding in the sandwich complexes has been a matter of great interest and some controversy since the synthesis of ferrocene in 1951. Various theoretical calculations[1-6] of the energy levels of ferrocene have led to different orders of the highest filled and lowest unfilled levels in this compound. One very sensitive test of these theoretical calculations is a check of the predicted orbital energy order against the order deduced by analysis of the absorption spectrum. Naturally, the validity of the orbital order deduced from the absorption spectrum depends upon the successful assignment of the absorption bands via some model. It is our object in this communication to make assignments for the weak absorption bands in the ferrocene spectrum and to determine the relative order of the *d* orbitals on the basis of a theoretical model. The model employed here is one which has had widespread success in complexes, the ligand field model.

The visible and near ultraviolet spectrum of ferrocene in ethanol shows weak bands** at 30.82 ($\varepsilon = 51$), 22.70 ($\varepsilon = 89$), 18.59 ($\varepsilon = 2.3$), 16.10 ($\varepsilon = 0.34$), and 14.2 ($\varepsilon = 0.16$) kK. The last two features occur as very weak shoulders on the tail of the 22.70 kK band. These bands may be reasonably assigned as ligand field bands involving transitions between the Fe^{2+} *d* levels split by the perturbing field of the $C_5H_5^-$ ligands[2]. The one-electron orbital energies of the *d* orbitals are[7,8]

$$E(a_{1g}) = 2Ds - 6Dt = E(d_0) = E(d_{z^2})$$
$$E(e^*_{1g}) = Ds + 4Dt = E(d_{\pm 1}) = E(d_{xz}, d_{yz})$$
$$E(e_{2g}) = -2Ds - Dt = E(d_{\pm 2}) = E(d_{x^2-y^2}, d_{xy})$$

where Ds and Dt are the splitting parameters as defined by Piper and Carlin[8]. The ground state *d* configuration of ferrocene is assigned to be $(a_{1g})^2(e_{2g})^4$ [$^1A_{1g}$] in agreement with the majority of calculations and overlap considerations. The one-electron excitations $a_{1g} \rightarrow e_{1g}{}^*$ and $e_{2g} \rightarrow e_{1g}{}^*$ produce excited states $^{1,3}E_{1g}$ (1) and $^{1,3}E_{1g}$ (2); $^{1,3}E_{2g}$ respectively. Note that configuration interaction will mix the two $^1E_{1g}$ states and also the two $^3E_{1g}$ states. We denote the higher energy components of this mixing as $^{1,3}E_{1g}{}^+$ and the lower energy ones as $^{1,3}E_{1g}{}^-$. In the ligand field model the excitation energies from the ground state to these excited states may be expressed in terms of the one-electron orbital energies and the Slater–Condon parameters F_2 and F_4.

Since there are only four parameters, Ds, Dt, F_2, and F_4, and five experimental bands (actually six since two unresolved bands occur near 22.7 kK), we need make no assumptions about the values of any of the parameters. We may determine their values from the experimental data and even make predictions as to the locations of

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* Abstracted from the Ph.D. Dissertation of D. R. Scott, University of Houston, Houston, Texas, Jan., 1965. National Science Foundation Cooperative Predoctoral Fellow, 1962–1963; present address: Department of Chemistry, Texas Technological College, Lubbock, Texas. Supported in part by the Robert A. Welch Foundation of Houston, Texas.

** The maxima and ε values of the last three bands reported were obtained by a Gaussian resolution and are corrected for the tail of the overlapping 22.7 kK band.

two bands. A very successful overall fit to all of the experimental data is given with the following values for the parameters: $Ds = 4960\ \mathrm{cm}^{-1}$, $Dt = 3050\ \mathrm{cm}^{-1}$, $F_2 = 923\ \mathrm{cm}^{-1}$, and $F_4 = 103\ \mathrm{cm}^{-1}$ (see Table 1). The standard deviation between the calculated and observed band maxima for all six bands is 260 cm^{-1}. The assignments of the ligand field bands are: ${}^1A_{1g} \rightarrow {}^1E_{1g}^{+}$ (30.82 kK); ${}^1E_{2g}$ and ${}^1E_{1g}^{-}$ (22.70 kK); ${}^3E_{1g}^{+}$ (18.59 kK), ${}^3E_{2g}$ (16.10 kK) and ${}^3E_{1g}^{-}$ (14.2 kK). (The numerical data in parentheses are the experimental data.) Note that the experimental band with maximum at 22.70 kK is composed of the two experimentally unresolved overlapping transitions, ${}^1E_{2g}$, ${}^1E_{1g}^{-}$*.

TABLE 1

CALCULATED AND EXPERIMENTAL LIGAND FIELD BANDS OF FERROCENE

Transition	*Experimental*[a]		*Calculated*[b]
	ν_0 (*kK*)	ε_0	ν_0 (*kK*)
${}^1A_{1g} \rightarrow {}^1E_{1g}^{+}$	30.82 ± 0.04	51	30.82
${}^1E_{2g}$	22.70 ± 0.03	89	22.85
${}^1E_{1g}^{-}$			22.54
${}^3E_{1g}^{+}$	18.59 ± 0.26[c]	2.3[c]	18.83
${}^3E_{2g}$	16.10 ± 0.22[c]	0.34[c]	15.64
${}^3E_{1g}^{-}$	14.2 ± 0.30[c]	0.15[c]	14.39

[a] Experimental data in ethanol. [b] $Ds = 4960\ \mathrm{cm}^{-1}$; $Dt = 3050\ \mathrm{cm}^{-1}$; $F_2 = 923\ \mathrm{cm}^{-1}$; $F_4 = 103\ \mathrm{cm}^{-1}$. [c] These data are corrected for the tail of the overlapping 22.7 kK band.

The excellent agreement between our calculated and experimental data gives us confidence that these weak bands in the absorption spectrum of ferrocene are ligand field bands as was suggested previously[2,10] and are not charge transfer bands as suggested by some authors[4]. The one-electron orbital energies may be calculated from the fitted values of *Ds* and *Dt*, and the energy differences between these determined. The order of the *d* levels is found to be $e_{1g}^* > a_{1g} > e_{2g}$ with $e_{1g}^* - a_{1g} = 25.5$ kK and $a_{1g} - e_{2g} = 4.59$ kK. This order of the levels is in qualitative and semi-quantitative agreement with the semi-empirical MO calculations carried out via the Wolfsberg–Helmholz approximation[5,6,11] but does not agree with the order predicted by the SCF calculations[3,4]. Thus the Wolfsberg–Helmholz calculations yield the correct order of the *d* levels in this compound. The previously noted good agreement[2] between the experimental spectrum and an incomplete ligand field calculation[12] now appears to be fortuitous. The fitted values of F_2 and F_4 allow us to compute the nephelauxetic parameter, $\beta = [F_2 - 5F_4\ (\text{complex})]/[F_2 - 5F_4\ (\text{free ion})]$, for ferrocene. Using B(free ion)[13] for $\mathrm{Fe}^{2+} = 1058\ \mathrm{cm}^{-1}$, we obtain $\beta = 0.39$. This value places the $C_5H_5^-$ ligand near or above CN^- in the nephelauxetic series.

The order of the *d* orbitals derived from the absorption spectrum is also in agreement with the sign of the electric field gradient in ferrocene as determined by magnetic perturbation of the nuclear energy levels in a Mossbauer study[14]. Further

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* Dave, Evans and Wilkinson (ref. 2, p. 521) reported a resolution of the 22.7 kK band into two components at 25 kK and 22.2 kK. However, we are unable to verify this resolution, and low temperature studies[9] do not support these findings either. These low temperature studies show only a sharpening of the 22.7 kK band and a shift of the maximum toward shorter wavelength, no resolution into two bands.

details of the analysis of the absorption spectra of ferrocene and other sandwich complexes as well as a discussion of the relationship of the results to the bonding in these compounds will be published in the near future.

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1 F. A. COTTON, ed., *Progress in Inorganic Chemistry*, Vol. I, Interscience, New York, 1959.
2 D. R. SCOTT AND R. S. BECKER, *J. Chem. Phys.*, 35 (1961) 516, 2246.
3 E. M. SHUSTOROVICH AND M. E. DYATKINA, *Dokl. Akad. Nauk SSSR*, 128 (1959) 1234; *Zh. Strukt. Khim.*, 1 (1960) 109.
4 J. P. DAHL AND C. J. BALLHAUSEN, *Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd.*, 33 (1961) 5.
5 L. L. LOHR, Ph.D. Dissertation, Harvard University, 1963.
6 R. D. FISCHER, *Theoret. Chim. Acta*, 1 (1963) 418.
7 A. D. LIEHR AND C. J. BALLHAUSEN, *Acta Chem. Scand.*, 11 (1957) 207.
8 T. S. PIPER AND R. L. CARLIN, *J. Chem. Phys.*, 33 (1960) 1208.
9 F. J. SMITH, J. K. SMITH AND S. P. MCGLYNN, *Rev. Sci. Instr.*, 12 (1962) 1367.
10 D. A. LEVY, Ph.D. Dissertation, Cambridge University, 1960.
11 D. R. SCOTT AND R. S. BECKER, unpublished studies.
12 F. A. MATSEN, *J. Am. Chem. Soc.*, 81 (1959) 2023.
13 J. S. GRIFFITH, *The Theory of Transition-Metal Ions*, Cambridge Univ. Press, Cambridge, 1961, p. 437.
14 R. L. COLLINS, *J. Chem. Phys.*, 42 (1965) 1072.

Received May 17th, 1965

J. Organometal. Chem., 4 (1965) 409–411

The catalytic alkaline cleavage of partially substituted methylsiloxanes

Several cleavage reactions of partially substituted organosiloxanes (I) are known[1–3]. All are characterised by strict stoichiometry between the reactants.

$R_mH_{(3-m)}SiOSiR_nH_{(3-n)}$ (I)

R = lower aliphatic or aromatic hydrocarbon radicals, identical or different

m, *n* = 1, 2 or 3, identical or different

We have now observed alkali-catalysed cleavage with hydrogen migration between silicon atoms of some siloxanes of type (I) with R = Me. The reaction produces silanes with increased H/Si ratio and siloxanes with increased O/Si ratio. The reactions were carried out under dry argon or nitrogen in dry ether or tetrahydrofuran containing 5% starting material and 1–100 parts per million of sodium. Examples of starting materials and products are listed in Table 1.

All products were identified by infrared spectroscopy[4], supplemented by gas-liquid chromatography for the gaseous silane mixtures. Nuclear magnetic resonance spectroscopy was used to check the purity of the starting materials. Sodium was determined by flame photometry in the residue after evaporation of 500 ml solvent containing concentrated hydrochloric acid.

Tetrahydrofuran dissolves up to 0.5 parts per million of sodium out of glass, enough to catalyse the cleavage reactions. No reaction was found in quartz apparatus with solvents containing less than 0.01 part per million of sodium.

The same cleavage also occurs in hydrocarbons above 100° in the presence of sodium metal if the solution contains about 50 parts per million water or lower alcohol, but there is no reaction if this quantity is less than 10 parts per million.