Inorganica Chimica Acta, 9 (1974) 209–212

The Mössbauer Investigation of Some Derivatives of Ferrocenes

L. KORECZ, H. ABOU
Department of Atomic Physics L. Eötvös University, Budapest, Hungary
G. ORTAGGI
Istituto Chimico, Università, Roma, Italy
M. GRAZIANI, U. BELLUCO
Istituto Chimica Generale, Università, Venezia, Italy
K. BURGER
Department of Inorganic and Analytical Chemistry L. Eötvös University, Budapest, Hungary
Received September 21, 1973

The Mössbauer parameters of a series of ferrocene derivatives has been determined. The isomer shift values were independent from the nature of the substituent on the cyclopentadiene ring. The differences in the quadrupole splitting values served informations on the changes caused by the substituents in the electronic structure of the iron central atom. The Mössbauer parameters were interpreted on the basis of MO–LCAO–SCF calculations of Shustorovich and Dyatkina. Our results were found in better accord with these than with the analogous calculations of Dahl and Ballhausen.

Introduction

The Mössbauer spectra of ferrocene and some of its derivatives have been determined by several groups.[1–8] Theoretical calculations dealing with the electronic structure of ferrocene are also published in the literature.[9–11]

Previous Mössbauer investigations have shown that the substitution of hydrogen atoms in the cyclopentadiene ring did not cause significant changes in the isomer shift δ of the complex. Neither did oxidation to ferrocinium ion cause any considerable change in δ.

The aim of our investigation was to get further information on the effect of different substituents on the electronic structure of the iron central atom of ferrocene. The Mössbauer parameters of a series of monosubstituted ferrocene derivatives have been determined. Four of the compounds have been previously investigated.[2–4] The Mössbauer parameters of these, determined in our investigations, were found to be in good agreement with those published in the literature.

Experimental

The compounds have been prepared by the methods reported in the literature,[12] and characterized by elemental analysis and UV, visible and IR spectroscopy.

The Mössbauer spectra have been recorded by an apparatus constructed in the Atomic Physics Department of the L. Eötvös University[13] provided with a driving equipment of constant acceleration, using a ^{57}Co isotope diffused into a copper foil, made in the Radiochemical Centre, Amersham, England as source. The full line width at half height of this source was found to be 0.27 mm/sec against a sodium ferrocyanide absorber containing 0.25 mg ^{57}Fe/cm^2. Metallic iron of special high purity prepared by Reanal, Hungary especially for this purpose was used for the calibration of the velocity scale. The velocity scale was strictly linear. To check the velocity scale the spectrum of a standard $Na_2[Fe(CN)_5NO]$ was also recorded. The measurements were carried out at 80° K temperature. The Mössbauer parameters were evaluated by a computer curve fitting procedure.[19] The isomer shift values are referred to metallic iron at room temperature.

The Mössbauer spectrum of each compound was recorded in several independent experiments (more than 100000 gamma counts per point, and 25 points per 1.0 mm/sec in the spectra). The reproducibility of the Mössbauer parameters was found to be ±0.015 mm/sec. The statistical error of the computer evaluated parameter was found to be 0.002–0.004 mm/sec.

Results and Discussion

The Mössbauer parameters are shown in Table I. The isomer shift values of the derivates are equal within the experimental error to that of ferrocene, except

TABLE I. Mössbauer Parameters of the Ferrocene Derivatives.

	Isomer Shift δ mm/sec	Quadrupole Splitting ε mm/sec
1. $(C_5H_5)Fe(C_5H_4COCH_3)$ Acetylferrocene	0.53	2.24
2. $(C_5H_5)Fe(C_5H_4CH_2OH)$ Ferrocenetylmethanol	0.54	2.37
3. $(C_5H_5)Fe(C_5H_4CH(OH)(CH_3)$ Ferrocenetylethanol	0.54	2.32
4. $(C_5H_5)Fe(C_5H_4B(OH)_2)$ Ferrocene boronic acid	0.52	2.26
5. $(C_5H_5)Fe(C_5H_4HgBr)$ Bromomercury ferrocene	0.59	2.36
6. $(C_5H_5)Fe(C_5H_4CH_2\text{–}N^+(CH_3)_3)I^-$ Trimethylferrocenemethylammoniumjodid	0.50	2.30
7. $(C_5H_5)Fe(C_5H_4I)$ Iodoferrocene	0.54	2.44
8. $(C_5H_5)Fe(C_5H_4Br)$ Bromoferrocene	0.53	2.46
9. $(C_5H_5)Fe(C_5H_4Cl)$ Chloroferrocene	0.54	2.40
10. $(C_5H_5)Fe(C_5H_4COOH)$ Ferrocene carboxilic acid	0.53	2.21
11. $(C_5H_5)Fe(C_5H_5)$ Ferrocene	0.53	2.37

for compounds 5 and 6; the quadrupole splitting values span a velocity range of 0.25 mm/sec.

With a knowledge of the molecular orbitals of the complexes the theoretical values of the Mössbauer parameters could be calculated. Since the MO–LCAO–SCF calculations of Shustorovich and Dyatkina[9] and those of Dahl and Ballhausen[10] gave contradictory results (see Table II), we computed the Mössbauer isomer shift of ferrocene on the bases of both calculations using the Walker–Jaccarino–Wertheim diagram[14] modified by Korecz.[15]

According to the MO–LCAO–SCF calculations of Shustorovich and Dyatkina the electronic structure of iron in ferrocene has to be considered $3d^{5.44}$, $4s^{0.48}$, $4p^{1.41}$ and using the Fermi–Segré–Goudsmith formula[16,17] the 4s electron density at the iron nucleus is 1.35 a_o^{-3} (where a_o represents the first Bohr radius of the hydrogen atom).

Analogous calculations of Dahl and Ballhausen have given however the electronic configuration $3d^{6.05}$, $4s^{0.80}$, $4p^{1.84}$ and the 4s electron density at the iron nucleus is 0.80 a_o^{-3}.

TABLE II. The Molecular Orbitals of Ferrocene According to Calculations of Shustorovich–Dyatkina,[9] and Dahl–Ballhausen.[10]

Molecular Orbitals According to Ref. 9	No. of Electrons	Metal Coefficient^2	Molecular Orbitals According to Ref. 10	No. of Electrons	Metal Coefficient ^{2}
$\psi_1(a_{1g}) = 0.49\psi_{4s} + 0.87\varphi_{a_{1g}}$	2	0.2401	$\psi_1(a_{1g}) = 0.633\psi_{4s} + 0.77\varphi_{a_{1g}}$	2	0.4007
$\psi_2(a_{1g}) = 1\psi_{3d_{z^2}}$	2	1.0000	$\psi_2(a_{1g}) = 1\psi_{3d_{z^2}}$	2	1.0000
$\psi_3(a_{2u}) = 0.1\psi_{4p_z} + 0.99\varphi a_{1u}$	2	0.0100	$\psi_3(a_{2u}) = 0.471\psi_{4zp_z} + 0.882\varphi_{a_{1u}}$	2	0.2218
$\psi_4(e_{1u}) = 0.59\psi_{4p_x} + 0.81\varphi e_{1u}$	4	0.3481	$\psi_4(e_{1u}) = 0.591\psi_{4p_x} + 0.807\varphi_{e_{1u}}$	4	0.3493
$\psi_5(e_{1u}) = 0.59\psi_{4p_y} + 0.81\varphi e_{1u}$	4	0.3481	$\psi_5(e_{1u}) = 0.591\psi_{4p_y} + 0.807\varphi_{e_{1u}}$	4	0.3493
$\psi_6(e_{1g}) = 0.37\psi_{3d_{xz}} + 0.93\varphi e_{1g}$	4	0.1369	$\psi_6(e_{1g}) = 0.454\psi_{3d_{xz}} + 0.891\varphi_{e_{1g}}$	4	0.2061
$\psi_7(e_{1g}) = 0.37\psi_{3d_{yz}} + 0.93\varphi e_{1g}$	4	0.1369	$\psi_7(e_{1g}) = 0.454\psi_{3d_{yz}} + 0.891\varphi_{e_{1g}}$	4	0.2061
$\psi_8(e_{2g}) = 0.85\psi_{3d_{xy}} + 0.52\varphi e_{2g}$	4	0.7225	$\psi_8(e_{2g}) = 0.898\psi_{3d_{xy}} + 0.440\varphi_{e_{2g}}$	4	0.8064
$\psi_9(e_{2g}) = 0.85\psi_{3d_{x2-y2}} + 0.52\varphi e_{2g}$	4	0.7225	$\psi_9(e_{2g}) = 0.898\psi_{3d_{x2-y2}} + 0.440\varphi_{e_{2g}}$	4	0.8064

The calculated isomer shift was found using the electronic structure got by the calculation of Shustorovich and Dyatkina ≃ 0.6 mm/sec and ≃ 1.1 mm/sec on the basis of the calculations of Dahl and Ballhausen. (Experimental values: 0.53 mm/sec). Thus, the good agreement of the experimental isomer shift with the former calculated one supports the correctness of the calculations of Shustorovich and Dyatkina.

Estimating the contribution of the p and d electrons to the electric field gradient, the value of the quadrupole splitting could be also estimated[18] on the basis of the cited MO–LCAO–SCF calculations. Using the results of the calculations of Shustorovich and Dyatkina the quadrupole splitting was found to be 2.2 mm/sec, but using Dahl and Ballhausen's data 2.9 mm/sec (experimental value: 2.37 mm/sec).

Since the experimental values were in better accord with the calculations of Shustorovich and Dyatkina than with those of Dahl and Ballhausen*, in our further computations only the former data have been used.

From the Mössbauer parameters the changes in the distribution of the electrons on the different d orbitals could be calculated. Knowing that the electric field gradient EFG of ferrocene has a positive sign[1] the increase of quadrouple splitting indicates the increase of the number of electrons in the orbitals giving a positive contribution to the EFG and/or the decrease of electron population orbitals giving a negative contribution to the EFG. A decrease of quadrupole splitting indicates the opposite electronic process. Considering the isomer shifts to be equal in all investigated derivates (which is in agreement with the experimental results and with the MO calculations of Shustorovich and Dyatkina showing that the overall population of 3d, 4s, and 4p orbitals is, even in ferrocinium ion, almost equal with that of ferrocene), from the differences of the quadrupole splittings of the substituted ferrocenes from that of ferrocene the parameters characteristic for the changes in the number of electrons of iron in the $d_{x^2-y^2}$, d_{xy} and in the d_{xz}, d_{yz} orbitals respectively, could be calculated. The data are compared in Table III. It is to be seen that the substitution of the hydrogen by halides decreases the number of electrons in the d_{xz} and d_{yz} orbitals and increases that in the $d_{x^2-y^2}$ and d_{xy} orbitals. The $-COOH$, $-COCH_3$, $-B(OH)_2$ and $-C(OH)CH_3$ groups, in contrast, increases the number of electrons in the d_{xz} and d_{yz} orbitals and decreases it in the $d_{x^2-y^2}$ and d_{xy} orbitals. It must be emphasized however that these are only minute changes. These small changes could be due also to distortions in the symmetry of ferrocene caused by the substituents.

The electronic density at the iron nucleus remain unchanged although the electronegativity of the ring substituents changes drastically. According to the MO calculations cited above an electron transfer of both directions is possible: from the metal to the cyclopentadienyl ring and also from the ring to the metal, *i.e.* the π-cyclopentadienyl ring has donor–acceptor properties and may behave as an electron reservoir in both directions internally balancing the effect of the substituents on the electronic density at the central atom.

TABLE III. Changes in the Number of Electrons in the d Orbitals of the Iron Central Atom.[a]

Complex	d_{xy} $d_{x^2-y^2}$	d_{xz} d_{yz}
$(C_5H_5)Fe(C_5H_4COCH_3)$	−0.02	+0.02
$(C_5H_5)Fe(C_5H_4CH_2OH)$	+0.00	+0.00
$(C_5H_5)Fe(C_5H_4CH(OH)CH_3)$	−0.01	+0.01
$(C_5H_5)Fe(C_5H_4B(OH)_2)$	−0.02	+0.02
$(C_5H_5)Fe(C_5H_4I)$	+0.01	−0.01
$(C_5H_5)Fe(C_5H_4Br)$	+0.02	−0.02
$(C_5H_5)Fe(C_5H_4Cl)$	+0.01	−0.01
$(C_5H_5)Fe(C_5H_4COOH)$	−0.03	+0.03

[a] The number of the electrons in the non bonding d_{z^2} orbital is considered constant.

The changes caused by the substituents in the electron distribution among the 3d orbitals of different spatial arrangement might be due to several different, possibly steric effects. Their deeper understanding needs further informations about the system.

References

1 R.L. Collins, *J. Chem. Phys.*, *42*, 1072 (1965).
2 G.K. Wertheim and R.H. Herber, *J. Chem. Phys.*, *38*, 2106 (1963).
3 A.V. Lesikar, *J. Chem. Phys.*, *40*, 2746 (1964).
4 R.A. Stukan, S.P. Gubin, A.N. Nesmeyanov, V.I. Goldanskii and E.F. Makarov, *Teor. i eksp Khim.*, *2*, 805 (1966).
5 R.E. Dewames and G.W. Lehman, *Phys. Rev.*, *135*, A170 (1964).
6 N.E. Alekseevskii, F. Zuy Hien, V.G. Shapiro and V.S. Shpinel *Zh. Eksperim. i. Theor. Fiz.*, *43*, 790 (1962). Engl. Transl: *Soviet Phys. JETP*, *16*, 559 (1963).
7 C.J. Meecham and A.H. Muir, *Rev. Mod. Phys.*, *36*, 438 (1964).
8 U. Zahn, P. Kienle and H. Eicher, *Z. Phys.*, *166*, 220 (1962).
9 E.M. Shustorovich and M.E. Dyatkina, *Dokl. Akad. Nauk. SSSR*, *128*, 1234 (1959); *Zhur. Strukt. Khim.*, *1*, 109 (1960).
10 J.P. Dahl and C.F. Ballhausen, *Mat. Fys. Medd. Dan. Vid. Selks.*, *33*, No. 5 (1961).
11 Y.S. Sohn, D.N. Hendrickson, and H.B. Gray, *J. Am. Chem. Soc.*, *93*, 3603 (1971) and references therein.
12 M. Rosenblum, *Chemistry of the Iron Group Metallocenes*, Part One, Interscience, 1965; D.E. Bubblitz and K.L. Rinehart, Ir., *Organic Reactions*, *17*, 1 (1969).

---

* The experimental fact that ferrocene and ferrocinium ion have almost identical isomer shift values[2] is also a direct proof of the correctness of the data of Shustorovich and Dyatkina.

13 K. Burger, L. Korecz, P. Mag, U. Belluco and L. Busetto, *Inorg. Chim. Acta, 5,* 362 (1971).
14 L. R. Walker, G.K. Wertheim and V. Jaccarino, *Phys. Rev. Letters., 6,* 98 (1961).
15 L. Korecz, *Proc. Conf. Appl. Mössbauer Effect,* Tihany, 1969. Publ. House of the Hungarian Academy of Sciences, Budapest, 1971, p. 725.
16 E. Fermi and E. Segré, *Z. Phys., 82,* 729 (1933).
17 S. A. Shirley, *Rev. Mod. Phys., 36,* 339 (1964).
18 N. N. Greenwood and T. C. Gibb, *Mössbauer Spectroscopy,* Chapman–Hall, London, 1971, p. 235.
19 K. Kulcsár, D.L. Nagy and L. Pócs, *Proc. Conf. Mössbauer Spectrometry,* Dresden, Vol. 2, p. 594 (1971).