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SUBSTITUENT EFFECT IN KETOFERROCENES

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BUDAPEST

SUBSTITUENT EFFECT IN KETOFERROCENES

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ABSTRACT

The effect of carbonyl-group on the redox potential and Mössbauer para-
meters was studied in ketoferrocenes and chalcone analogous ferrocene deriva-
tives. Interaction of electron-donating and electron-withdrawing substituents
and the carbonyl-group is discussed and the transmission coefficient of the
ethylene is shown. The effect of carbonyl on the population of the molecular
orbital is discussed on the basis of Mössbauer measurements.

АННОТАЦИЯ

Методом мессбауэровской спектроскопии и циклической вольтамметрии про-
водились исследования роли карбонильных радикалов в кетоферроценах и произ-
водных ферроцена, являющихся аналогами хальконов. Показано модифицирующее
влияние включающихся в карбонильные группы прочих нуклеофильных и электро-
фильных заместителей, а также определяется трансмиссионный коэффициент эти-
леновой группы. На основе мессбауэровских параметров исследовалось влияние
карбонильных групп на популяцию молукулярных обриталей.

KIVONAT

Ketoferrocénekben és chalconokkal analóg ferrocén származékokban vizs-
gáljuk a karbonilgyök szerepét Mössbauer spektroszkópia és ciklikus voltam-
metria segitségével. Bemutatjuk a karbonil-csoporthoz kapcsolódó egyéb nuk-
leofil és elektrofil szubsztituensek módositó hatását, valamint az ethylén
-csoport transzmissziós köefficiensét. Mössbauer paraméterek alapján foglal-
kozunk a karbonil-csoport molekula-pálya (MO) populációt módositó hatásával.

INTRODUCTION

In the early years of ferrocene chemistry it was revealed that reversible one-electron oxidation of ferrocene to the ferricenium cation was a characteristic reaction of the molecule [1,2]. This reversible oxidation is effected chemically, anodically or photolytically [3,4]. The ease of oxidation of ferrocene derivatives was found to be related to the electronic character of the substituents in the cyclopentadienyl rings, thus electrondonating substituents decreased the oxidation potential whereas the electron-withdrawing groups had the opposite effect [5-9]. Many research teams have provided correlations of redox potentials with various properties of the substituted ferrocenes [10-13]. Analysis of the results showed that the oxidation potentials of the ferrocene derivatives were sensitive to structural and conformation effects as well. For example, a correlation was found between the change in molecular geometry and the redox potentials as well as the Mössbauer parameters of bridged ferrocenes [14,15]. In the present paper the interaction of some substituents is studied by Mössbauer spectroscopy and cyclic voltammetry in several keto derivatives of ferrocene.

EXPERIMENTAL

Methods. The Mössbauer spectra of these compounds were recorded at room temperature by means of a constant acceleration spectrometer using a ^{57}CO source in a chromium matrix. The Mössbauer parameters were evaluated by the least squares method. Metallic iron was used for the calibration of the velocity scale. From three to five measurements were made for each sample. The relative errors of QS and IS values are given in Table II.

Electrode Potential Measurements. Electrode potentials for the one-electron oxidation of the ferrocenes to their respective cations were measured by cyclic voltammetry [16]. A three-electrode cell was used in which the working and auxiliary electrodes were platinum and the reference electrode was Ag/AgCl (sat). The solutions were 0.1 mole tetrabutylammonium perchlorate in acetonitrile which had been dried over molecular sieves. The potentiostat (type OH-105) was a Radelkis (Hungary) product. The measurements were made at a scan rate of 66 mV/s. Ferrocene and phenylferrocenylketone were used as internal standards to eliminate systematic errors. The utilization of internal standards increases the accuracy of cyclic voltammetry [17,18].

Materials. Ferrocene analogues of chalcones were prepared by base catalysed aldol condensation according to Ref. [19]. These compounds were purified by repeated crystallization from ethanol. Purities of compounds were checked by their melting points, thin layer chromatography (TLC) and IR spectra. The monoacetylferrocene was prepared by the method of Rosenblum [20]. It was purified by sublimation. Purity was checked by its melting point and TLC. Except for the phenyl-ferrocene all the other compounds were purchased from Ventron Corporation. The phenylferrocene was donated by Prof. S. Toma.

Results and Discussion

The oxidation potentials ($E_{1/2}$) and the Mössbauer parameters of the ferrocene derivatives studied are listed in Tables I and II. The schemes of the ketoferrocenes are shown in Fig.1. It can be seen that the $E_{1/2}$ value of 3-aryl-1-ferrocenyl-2-propene-1-one is considerably higher than that of the ferrocene. The carbonyl -group in the α position in relation to the cyclopentadienyl ring increases significantly the redox-potential of the iron component in the ferrocenyl moiety. Considering the $E_{1/2}$ of the monoacetylferrocene (Table I) we can see that the $E_{1/2}$ values of these two compounds are very near to each other which means that the double bond between the C_α and C_β and the phenyl group localized far from the ferrocenyl are not able to modify significantly the effect of the carbonyl-group on the ferrocenyl moi-

ety. This is also confirmed by the $E_{1/2}$ value of phenylferro-
cenylketone (689 mV) which surpasses the redox potentials of the
monoacetylferrocene and the 3-aryl-1-ferrocenyl-2-propene-1-one
by only a few mV. The phenyl group itself is a relatively weak
electron-withdrawing substituent which decreases the $E_{1/2}$ of
ferrocene by 33 mV (see Table I).

If we compare the $E_{1/2}$ values of the three ferrocene derivatives
it is obvious that, in spite of the small ΔE values, the trend
of the redox potentials is in good agreement with the properties
of the substituents, i.e. that the phenyl-group is an electron-
withdrawing substituent and the methyl-group is an electron-
donating one.

The $E_{1/2}$ of 1-aryl-3-ferrocenyl-2-propene-1-one surpasses
the $E_{1/2}$ of the ferrocene by 123 mV (Table 1). Consequently the
carbonyl group is able to influence the ferrocenyl-moiety even
via the double bond. According to our measurements the transmis-
sion coefficient of the double bond is 0.501. This value is in
good agreement with the transmission coefficient (0.51) obtained
by ^{1}H NMR measurements of chalcones [21]. Thus ~50% of the induc-
tive effect of the carbonyl can reach the ferrocenyl through
the ethylene.

The chemical shifts of H_α and C_α in both compounds (Fig.1)
were found at higher fields than those of H_β and C_β, similar to
the chemical shifts found for the benzene chalcones in their H^1
and C^{13} NMR spectra [22,23]. This is caused by the polarization
of the double bond by the carbonyl group. The chemical shifts of
C_β in the 3-aryl-1-ferrocenyl-2-propone-1-one and H_α and C_α in
1-aryl-3-ferrocenyl-2-propene-1-one are at higher fields than in
the analogous benzene chalcones, explainable by the strong elec-
tron-donating character of the ferrocenyl group [24].

In our previous work on the keto derivatives of bridged
ferrocenes it was suggested that consideration be given to the
different contributions of the bridges without ketone to the
redox potentials [17]. In the case of monoacetylferrocene, for
example, the ΔE value is 287 mV if, instead of the ferrocene $E_{1/2}$,
the potential of ethylferrocene is considered when calculating
of ΔE value. The ethyl group thus donates 55 mV [17]. The ΔE

value of 287 mV for the monoacetylferrocene is near to that of the carbonyl in ferrocenylcarbaldehyde and fits well with the set of ΔE values obtained in the keto derivatives of bridged ferrocenes [17]. In reality, such treatment of the results is possible only in a few cases because the reduced pair of keto ferrocenes is not always available.

According to the Mössbauer measurements the quadrupole splittings (QS) for all of these compounds (Fig.1) are found to be smaller than that of ferrocene whereas the isomer shifts (IS) remain the same or a little bit higher than that of the ferrocene. A similar effect of the carbonyl on the Mössbauer parameters was observed for the keto-derivatives of bridged ferrocenes as well [25]. These observations support the assumption that the electron-withdrawing effect of the carbonyl increases the population of the ϵ_1 /d_{xz}, $d_{yz}/$ molecular orbital (MO) [26]. According to MO calculations for ferrocene, the contribution of the ϵ_1 population to the QS value is -2.4 mm/s; the contribution of ϵ_2 /d_{xy}, $d_{x^2-y^2}/$ is +5.4 mm/s [27,28,29].

Accordingly a decrease in the ϵ_2 population should be accompanied by a decrease of IS because of the decreased shielding effect of "d" electrons on the "s" electron density at the nucleus [30]. Since the IS values of these compunds are higher than that of ferrocene it is probable that the ϵ_2 is not involved in the effect of the carbonyl group.
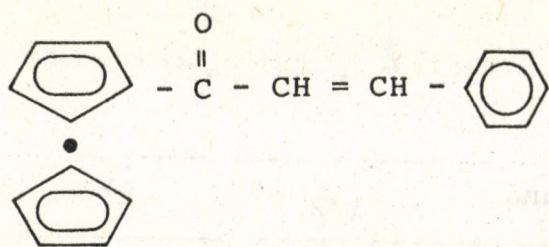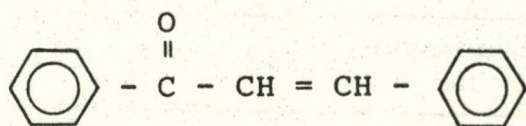
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\text{I. 3-aryl-1-ferrocenyl-2-propene-1-one}
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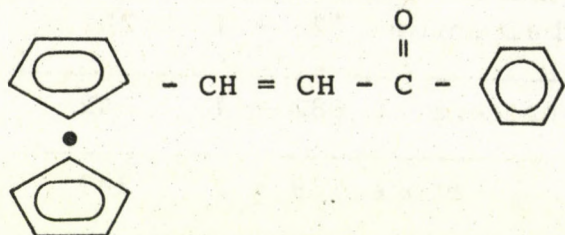
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\text{II. 1-aryl-3-ferrocenyl-2-propene-1-one}
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\text{III. 3-aryl-1-aryl-2-propene-1-one}
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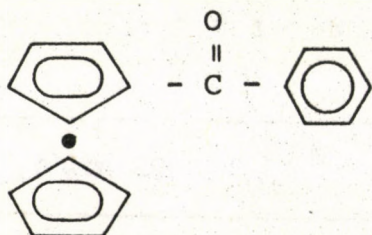
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\text{IV. ferrocenyl-phenyl-ketone}
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Fig.1. *The schemes of ferrocene derivatives studied*

Table 1. Redox potentials of keto-ferrocenes

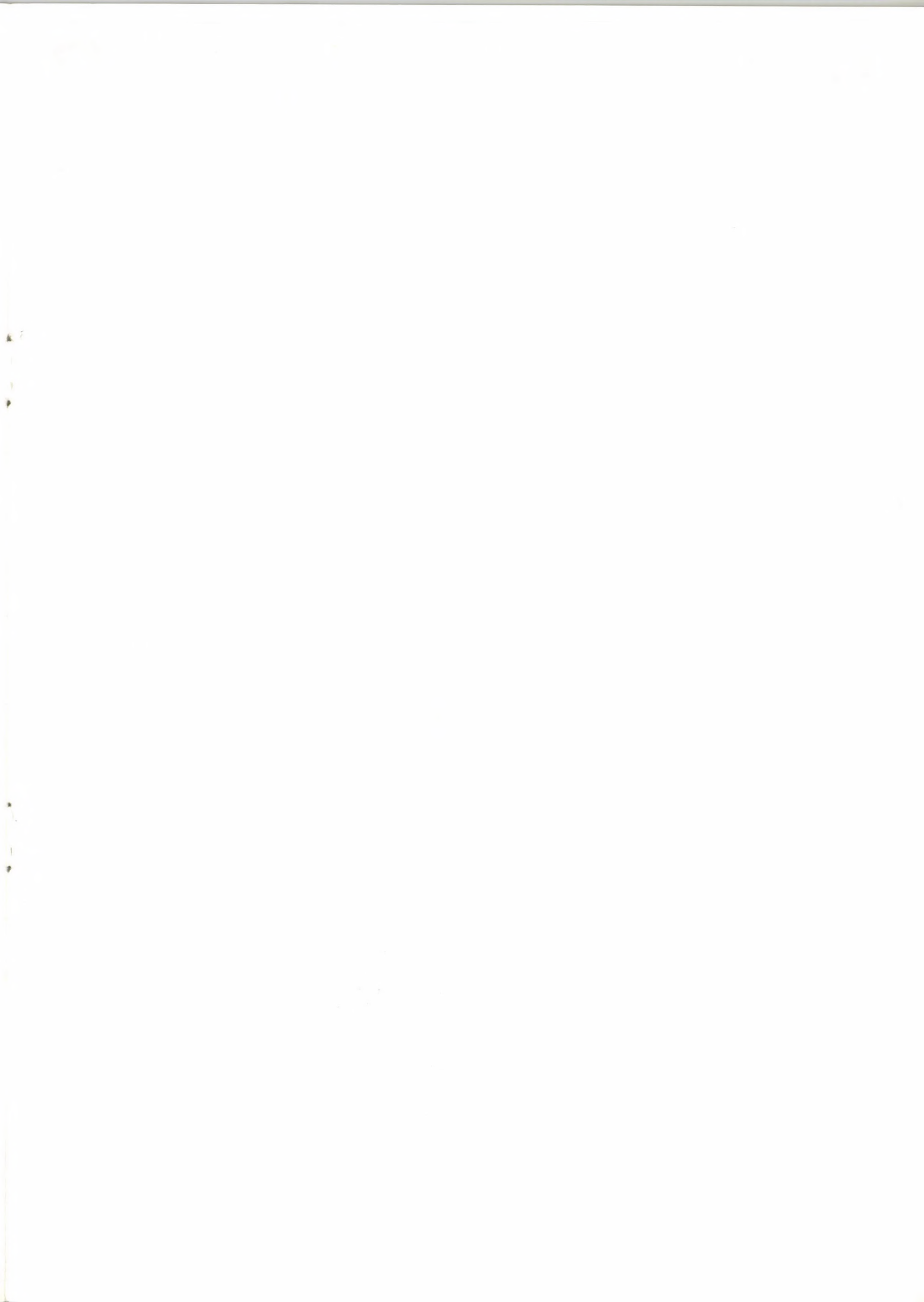| N_O	Compound	$E_{1/2}$ mV	ΔE
1.	Ferrocene	440 ± 1	-
2.	Ferrocenecarbaldehyde	723 ± 1	283
3.	Monoacetylferrocene	682 ± 1	242
4.	Ferrocenylphenylketone	689 ± 2	249
5.	3-aryl-1-ferrocenyl--2-propene-1-one	685 ± 1	245
6.	1-aryl-3-ferrocenyl--2-propene-1-one	563 ± 1	123
7.	Phenylferrocene	473 ± 1	33

Table 2. Mössbauer parameters of keto-ferrocenes

Compound	IS mm/s	$\Delta IS \cdot 10^3$	QS mm/s	$\Delta QS \cdot 10^3$
Ferrocene	0.432 ± 2	-	2.367 ± 2	-
Ferrocenecarbaldehyde	0.448 ± 1	+16	2.225 ± 2	-142
Monoacetylferrocene	0.434 ± 2	+2	2.263 ± 4	-104
Ferrocenylphenylketone	0.450 ± 1	+18	2.251 ± 1	-116
3-aryl-1-ferrocenyl--2-propene-1-one	0.447 ± 1	+15	2.223 ± 1	-144
1-aryl-3-ferrocenyl--2-propene-1-one	0.438 ± 2	+6	2.219 ± 5	-148
Phenylferrocene	0.445 ± 1	+13	2.297 ± 3	-70

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