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Two Types of Protons in Ferrocene

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Abstract—Two absorption bands of ferrocene, the in-plane bending C–H vibrations (β_{CH}) at 1002 cm^{-1} and out-of-plane C–H vibration (γ_{CH}) at 816 cm^{-1}, are accompanied with high-frequency satellites β_{CH} (1055) and γ_{CH} (837 cm^{-1}). In the spectrum of 1,1'-dideuteroferrocene, only the high-frequency bands suffer an isotopic shift, from 1055 to 859 cm^{-1}, and from 837 to 668 cm^{-1}. Only additional incorporation of deuterium into 1,1'-dideuteroferrocene results also in an isotopic shift of the basic bands: 1002 to 771 and 816 to 632 cm^{-1}. Therefore, one of the five carbon atoms of cyclopentadienyl ring of ferrocene differs from the other in the static state. It is assumed that just this carbon atom is bonded with the iron atom by the σ-bond.

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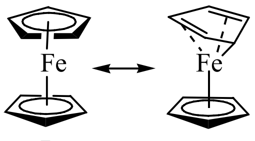
The structure of ferrocene may be represented as a π-complex of two cyclopentadienyl anions. The problem is whether the initial σ-bond remains or disappears (delocalizes). The equivalence of all hydrogen atoms in the ^{1}H NMR spectrum does not give an answer to this question, since the indubitable ionic cyclopentadienyl metal complexes, for example dicyclopentadienyl mercury, also contain one signal in the ^{1}H NMR spectrum.

By X-ray diffraction data, the distances between carbon and iron atoms are approximately equal [1], attesting in favor of equivalence of the ring carbon atoms. Nevertheless, formally in ferrocene are combined both the σ- and π-bonds between the iron and the ring. It is difficult to represent or calculate quantum-mechanically how this occurs [2]. Poson supposed that σ-bond migrated continuously over the ring carbon atoms, but even in this case the presence of the σ-bond should be revealed. According to recent ferrocene calculation data [3], the separate σ- and π-bonding of the ring carbons with iron is considered as one of the resonance forms of the η^5 coordination.



I **II**

High stability of ferrocene served as a basis for adopting the formula **I**. The presence of one absorption band belonging to stretching CH vibrations (3080 cm^{-1}) also seemingly proves equivalence of all the carbon atoms. However, the second weak high-frequency absorption band at 3117 cm^{-1} was found (Fig. 1). When the in-plane and out-of-plane CH-vibrations are considered, not one but two bands are observed in each

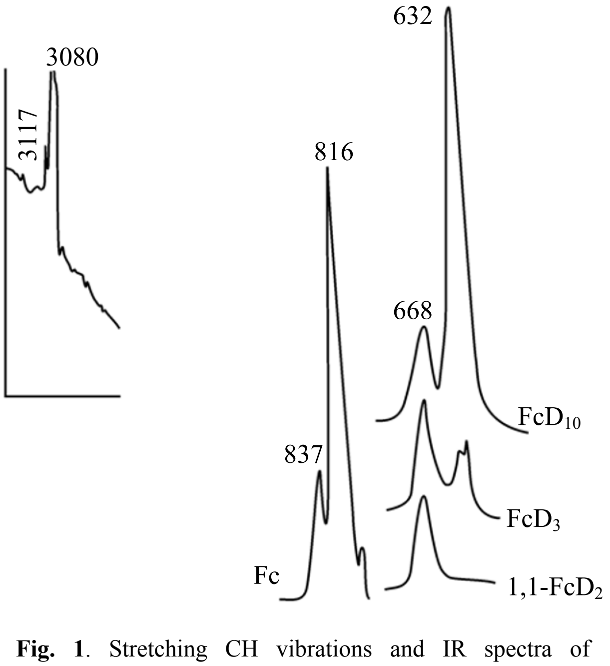


Fig. 1. Stretching CH vibrations and IR spectra of ferrocene and deuteroferrocenes in the field of out-of-plane CH and CD vibrations.

[†] Deceased.

of these vibrations. Furthermore, there are high-frequency satellites of these bands of low intensity at 1055 and 837 cm^{-1}.

Under the close examination and comparison of ferrocene and 1,1'-dideuteroferrocene spectra, the following pattern is seen (Fig. 2).

Ferrocene itself has two pairs of bands of in-plane vibrations (β_{CH}) at 1055 and 1002 cm^{-1} and out-of-plane vibrations (γ_{CH}) at 837 and 816 cm^{-1}. The spectrum and the assignment of the absorption bands were repeatedly discussed since the classic work of Lippincott and Nelson [4]. The presence of two absorption bands instead of one, as it should be evident from equivalence of all the C–H bonds, was never discussed and even was not noted as anomaly. Obviously, all the five equivalent ring hydrogen atoms must participate in each pairs of these vibrations. However, as it can be seen from the spectra, in 1,1'-dideuteroferrocene only the high-frequency bands of these pairs suffer an isotopic shift: from 1055 to 859 (index 1.23) and from 837 to 668 cm^{-1} (index 1.25). Consequently, the absorption bands at 1055 and 837 cm^{-1} belong only to one of the five protons of cyclopentadienyl ring. Only an additional incorporation of deuterium into the 1,1'-dideuteroferrocene (Fig. 1) causes a shift of the basic bands: from 1002 to 771, and from 816 to 632 cm^{-1} (index 1.29). In decadeuteroferrocene the two-band picture of ρ_{CH} is fully reproduced as two C–D bands at 669 and 632 cm^{-1}.

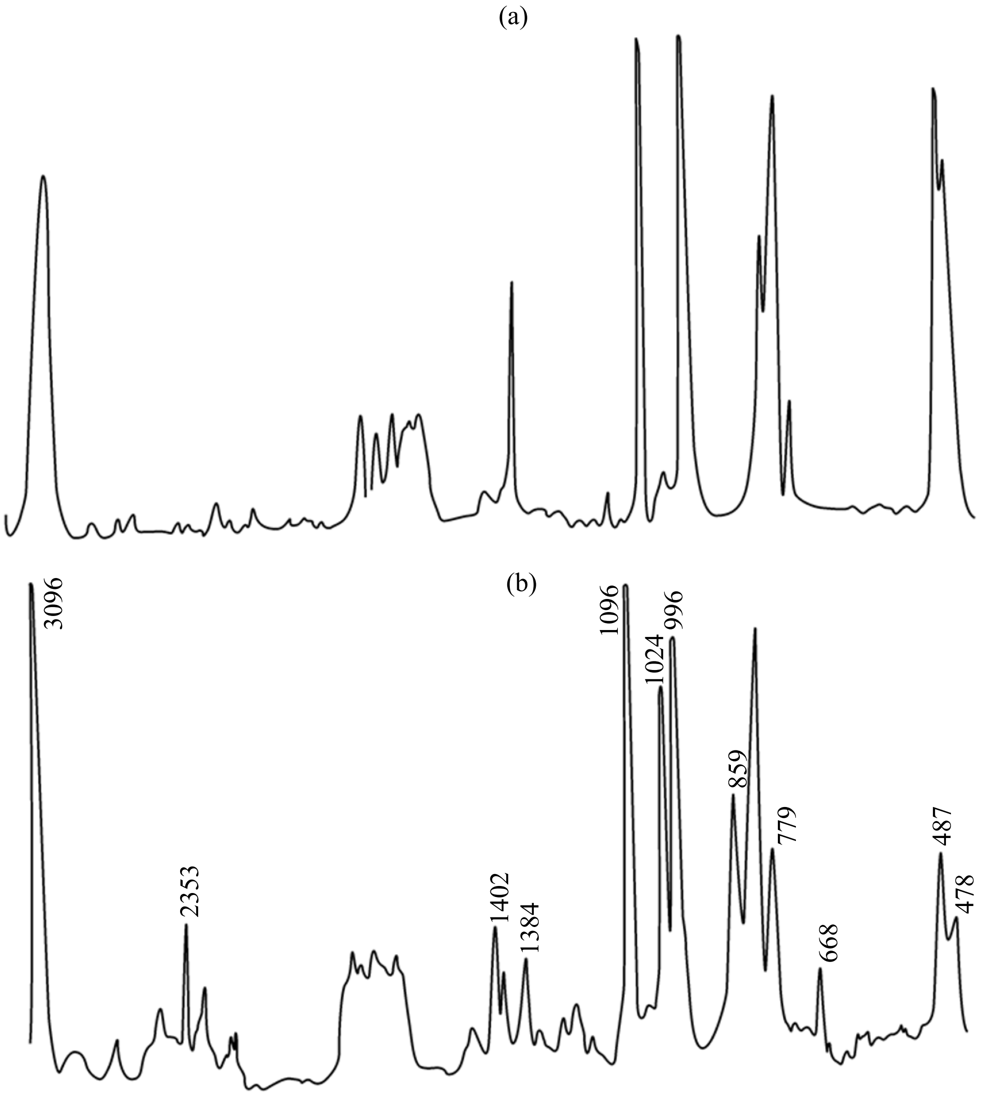
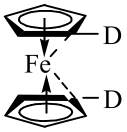


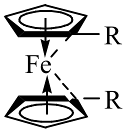
Fig. 2. (a) IR spectra of ferrocene and (b) 1,1'-dideuteroferrocene.

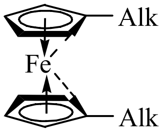
The higher frequencies of the bands β_{CH} 1055 and γ_{CH} 837 cm^{-1} can be interpreted as a decreased electron density on one of five carbon atoms of ferrocene ring. The only reason of all these data is the presence in the ferrocene, besides the π-bonding of iron with four carbon atoms, of an additional σ-bonding with the residual carbon atom (formula **III**).



III

The complete absence of absorption bands at 1055 and 837 cm^{-1} in the IR spectra of 1,1'-disubstituted ferrocenes (save alkylferrocenes) should be cited in favor of the difference in one of the five carbon atoms of ferrocene ring; in other words, the substituent in these compounds is located at this carbon atom, which is distinguished from the others. In the presence of the following substituents the absorption bands at 1055 and 837 cm^{-1} are absent in the spectra of substituted rings: OMe, OAc, SMe, SCN, Hlg, NHAc, NO_2, CN, Ac. Halogen-substituted rings have no bands at 1055 and 837 cm^{-1}. The deuteration of these compounds does not lead to appearance of deuterium at the σ-bonded carbon atom. The spectrum of 1-chloro-2-deuteroferrocene contains absorption band γ_{CD} at 650 cm^{-1} corresponding to the isotope shift of ρ_{CH} from 820 cm^{-1} (index 1.26). The deuterated ferrocene obtained by isotope exchange with deuterotrifluoroacetic acid (FcD_3 in Fig. 1) is interesting due to the fact that first of all the deuteron attacks the carbon bonded with iron through the σ-bond. Others reactions, for example, acylation and metallation, also involve this carbon atom. In a series of the heteroatomically substituted rings with such substituents as halogens, hyroxy-, alkoxy-, acetoxy- amino-, etc. the substituent always appears at the carbon atom σ-bonded with iron (**IV**).





IV **V**

It should be noted that electrophilic substitution at the ring containing these substituents failed since the most active position was already occupied. Chloroferrocene is acylated exclusively into the free ring [5] similarly to acylation of *N*-acetylaminoferrocene.

As a rule, the substituent enters into the substituted ferrocene ring only when the substituent is alkyl or analogous group (structure **V**) [1]. Alkylferrocenes differ spectrally from the derivatives containing a heteratomic substituent. IR spectra of alkylferrocenes, like the ferrocene itself, contain high-frequency satellites of the basic CH vibration bands at 1055 and 837 cm^{-1}. Moreover, the deuteration of 1,1'-diethylferrocene first of all leads to the appearance of isotopic shift of a band, the spectrum is shown in Fig. 1. Similar to 1,1'-dideuteroferrocene, deuterated alkylferrocenes absorb at 670 cm^{-1}. The absorption at 630 cm^{-1} also grows as deuterium content increases.

Therefore, there are two classes of the ferrocene derivatives. In the first class substituent is connected with the carbon atom σ-bonded with the iron (structure **IV**, heteroatomic substituents); in the second class there is a free C_σ–H bond (alkylferrocenes, **V**). The latter probably are a mixture of isomers (1,2 and 1,3) relative to the position of this bond to the substituent.

Just alkylferrocenes were involved into many electrophilic substitution reactions. The C–Fe bond is evidently unfavorable by energy if the carbon is connected with an alkyl, while a heteroatomic substituent and even deuterium strengthens this bond.

The high-frequency satellites of bands β_{CH} and γ_{CH} occur in the IR spectra of virtually all metallocenes. Furthermore, they are especially strong in ionic compounds containing C_σ–M bond. Apparently, the compounds of cymanthrene series and its derevatives also contain a localized σ-bond with manganese atom [1065 cm^{-1} (β_{CH}) and 878 cm^{-1} (γ_{CH})], but it is difficult to check a shift of these bands owing to deuteration since the range of 680–650 cm^{-1} is occupied by intensive absorption of carbonyl groups.

EXPERIMENTAL

1,1'-Dideuteroferrocene was obtained by procedure [5]. IR spectra were taken on IKS-14 and FSM-1201 instruments using cells for liquids with layer thickness of 0.01 cm, solvents CCl_4 and CS_2. Deuterium content was determined by the procedure [6] (excess water density at burning), and also by mass-spectrometry.

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